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# (The Journal of) Industrial and Engineering Chemistry

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VOLUME VI, 1914

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AT EASTON, PA.

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## TABLE OF CONTENTS

### EDITORIALS:

See Ourselves as Others See Us.....	2
The Index to Abstracts.....	2
The Balance of Trade in the Chemical Industries between the United States and Germany.....	2

### ORIGINAL PAPERS:

Synthetic Resins. By L. V. Redman, A. J. Weith and F. P. Brock.....	3
A Method for Determining the Amount of Zinc Chloride in Treated Wood. By Ernest Bateman.....	16
On the Composition of Giant Kelps. By A. R. Merz..	19
The Analysis of Complete Fertilizers Containing Cyanamid. By H. W. Hill and W. S. Landis.....	20
A Study of the Milk of Porto Rican Cows. By Howard J. Lucas and R. del Valle Sárraga and J. Román Benítez.....	22
A Study of American Grown Belladonna. By F. A. Miller and R. N. Reed.....	25

### LABORATORY AND PLANT:

An Investigation of the Explosion of a Sulfite Digester in the Paper Mills at Grand Mère, Quebec. By H. O. Keay.....	26
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### GERMAN OBSERVATIONS ON OUR INDUSTRIES:

What Did We Chemists Learn in America? By B. Rassow.....	32
Impressions of the Eighth International Congress of Applied Chemistry in New York and of Certain Fields of Industry in the United States. By Prof. Dr. D. Holde of Zehlendorf, Berlin.....	35

Travels through the United States in Conjunction with the Eighth International Congress of Applied Chemistry at New York, by Members of the Congress. By R. Hoffmann, of Clausthal.....	49
---	----

### AMERICAN INSTITUTE OF CHEMICAL ENGINEERS:

Sixth Annual Meeting—Transactions.....	70
The Effect of Legislation upon Chemical Industries—Presidential Address. By T. B. Wagner.....	71

### SCIENTIFIC SOCIETIES:

Tentative Specifications and Analytical Procedure for 30% Hevea Rubber Insulating Compound.....	75
---	----

### NOTES AND CORRESPONDENCE:

Ozone.....	82
Platinum Thief.....	83
Recovery of Iodine from the Waste Liquor in Copper Titrations.....	83

### PERSONAL NOTES.....

### BOOK REVIEWS:

Mineral and Aerated Waters; Technical Gas and Fuel Analysis; Die Verwendung der seltenen Erden; Principles of Agricultural Chemistry; Accident Prevention; Wissenschaftliche Grundlagen der Erdölbearbeitung..	84
--	----

### NEW PUBLICATIONS.....

### RECENT INVENTIONS.....

### MARKET REPORT.....

## EDITORIALS

### SEE OURSELVES AS OTHERS SEE US

American manufacturers and engineers are always keenly interested in the opinion of foreign experts regarding our industrial developments. It is by a self-analysis, based upon, or at least suggested by, such observations, that managers are often enabled to make substantial advances. Even lay suggestions often initiate changes or improvements which had previously been overlooked or considered infeasible. Comments on American industrial and social conditions by scientists and technologists learned in the industries of our greatest competitive nation will, we believe, amply justify this Journal in devoting the major portion of the present issue to such papers.

The Eighth International Congress of Applied Chemistry offered an unusual opportunity for chemists and chemical engineers from abroad to study our industrial systems. Prominent German technologists attended the congress as a matter of course and took an unusual interest in the large number of excursions arranged to show the industrial resources and plants of America.

A number of articles by these distinguished German experts who attended the Congress have recently appeared in Germany. From these, we have selected the papers by Professor Rassow, by Professor Hoffmann and by Professor Holde, and are publishing full translations in this issue of the Journal.

We are indebted to the *Zeitschrift für angewandte Chemie* for the original of Professor Rassow's address, and to the *Chemiker Zeitung* for the papers by Professor Hoffmann and by Professor Holde.

We believe the observations, conclusions, suggestions and criticisms coming direct from our well informed German guests will be found most interesting and instructive reading for American technologists and manufacturers.

### THE INDEX TO ABSTRACTS

The editors of *Chemical Abstracts* completed, on January first, the gigantic task of preparing, publishing and distributing to every member of the American Chemical Society, the index to Chemical Literature for the year 1913. How many members of this Society have stopped to consider the magnitude of this task? How many realize the amount of energy and the scope of the organization required to place this completed volume on our desks on the first day of the new year?

The index contains over eighty-two thousand titles, over 800 pages, and required seven and one half tons of paper for its production. The collection and arrangement of this material is a stupendous task, to say nothing of the problems involved in its production and distribution. Both the editors and printers of this volume should be congratulated and deserve the hearty approbation of every member of the chemical profession.

### THE BALANCE OF TRADE IN THE CHEMICAL INDUSTRIES BETWEEN THE UNITED STATES AND GERMANY

The belief is very widespread among the chemists and chemical merchants of this country as well as of Germany that the value of the imports of chemical products into the United States from Germany is very much greater than the value of the exports of chemical products from the United States into Germany.

Inspection of the tabulations of exports and imports of chemical products from and into Germany for the year 1904 (pp. 38-56 in "Die Chemische Industrie" by Gustav Mueller, published by Teubner at Leipzig in 1909) shows the balance of trade for that year to have been in favor of the United States to the extent of \$21,201,040; i. e., about \$1,800,000 per month or \$60,000 per day (the mark at 23.8c).

The following table has been compiled from the Mueller statistics referred to. It gives the various articles of export and import arranged in the order of their 1904 monetary value in round thousands, together with the percentage of total export or import of each article from or into Germany. It shows the total value of imports of 34 different articles into the United States from Germany to be \$16,993,200 or 15 per cent of the total exportation value of Germany's chemical products in 1904; also that the total value of exports of 21 different chemical products from the United States into Germany is \$38,194,240 or 24 per cent of the importation value of all the chemical products Germany imported in 1904. In other words, the United States takes 15 per cent of Germany's total foreign market in chemical products and in turn the United States supplies Germany with 24 per cent of its total imports of chemical products.

The two branches of chemical industry which are the greatest pride of Germany are the coal-tar color industry and the potash industry. In 1904 the combined export value of the products of these two industries to the United States was \$13,052,000 or 76.8 per cent of the total chemical exports to the United States; these are made up as follows:

Anilin and other dyes.....	\$4,358,000	
Alizarin.....	919,000	
Anilin oil and salt.....	904,000	
Indigo.....	823,000	
<b>COAL-TAR INDUSTRY.....</b>		<b>\$7,004,000</b>
Potassium chloride.....	2,820,000	
"Abraum" salts.....	1,683,000	
Sulfates of magnesium and potassium.....	1,164,000	
Potassium bicarbonate.....	381,000	
<b>POTASH INDUSTRY.....</b>		<b>6,048,000</b>
<b>Total.....</b>		<b>\$13,052,000</b>

This combined value is \$1,426,000 less than the U. S. shipments of refined petroleum to Germany in 1904. The value of the oleomargarine supplied to Germany in 1904 was 97.6 per cent of the value of anilin dyes supplied the U. S. and 60.7 per cent of the value of



Percentage of total export of product from Germany	U. S. Import from Germany	Value in U. S. dollars	Percentage of total export of product from Germany
20.7	Anilin and other dyes	14,478,000	85
		4,358,000	
		4,253,000	88.0
		4,001,000	80.0
		3,618,000	65.0
		2,837,000	79.4
59.5	Potassium chloride	2,820,000	
		2,680,000	
54.4	"Abraum" salts...	1,683,000	
		1,678,000	
		1,359,000	
58.0	Sulfates of magnesium and calcium	1,359,000	
26.0	Alizarin	904,000	
18.9	Anilin oil and salt	838,000	
		823,000	
16.5	Indigo	730,000	
		730,000	
31.4	Essential oils	424,000	
		424,000	
42.1	Potassium bicarbonate	374,000	
9.3	Palm oil, coconut oil and vegetable fats	326,000	
		326,000	
23.5	Quinine and its salts	288,000	
14.0	Alkaloids (exclusive of quinine), antipyrine and antifebrine	262,000	
24.0	Bronze and chrome colors	226,000	
55.8	Oxalic acid and potassium acid oxalate	205,000	
20.0	Potassium cyanide	195,000	
		181,000	
11.6	Lead pencils	178,000	
27.7	Bleaching powder	167,000	
		126,000	
24.0	Carbolic acid	124,000	
6.5	Zinc ashes	119,000	
15.1	Crude medicinals	112,000	
		112,000	
6.8	Chemical preparations for medicinal use	112,000	
11.7	Quebracho extract	112,000	
39.1	Barium salts	105,000	
24.4	Gelatin	105,000	
31.4	Tartar emetic and antimony preparations	102,000	
		97,000	
11.7	Salt	83,000	
11.6	Ozokerite, purified	81,000	
		74,000	
		67,000	
9.0	Glue	64,000	
		64,000	
		62,000	
12.1	Matches etc., exclusive of	55,000	
14.3	Ammonia, ammonium chloride and carbonate	55,000	
7.0	Lithopone	33,000	
7.7	Resins exclusive of	31,000	
10.8	Lake colors	31,000	
4.1	Ultramarine	31,000	
<b>TOTAL, \$16,993,200</b>			<b>TOTAL, \$38,194,240</b>

total coal-tar dye receipts in the U. S. from Germany. The acetate of lime account practically balances the indigo account. Out of the 21 classes of chemical products which Germany imported from the United States in 1904, 7 of them each made up 65 per cent and more of Germany's total importations of those articles; these seven are acetate of lime, oleomarga-

rine, refined petroleum, cotton seed oil, turpentine and other rosin oils, rosin and rock phosphate.

Figures later than 1904 are not conveniently available; there is no reason to suppose that there has, as yet, been a great shifting, if any, of the relative positions of any of the items herein involved.

BERNHARD C. HESSE

## ORIGINAL PAPERS

### SYNTHETIC RESINS

By L. V. BERMAN, A. J. WELCH and G. F. BROSCH

Received October 1, 1913

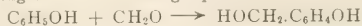
Condensation Products of Pyridine Bodies with Hexamethylene Diamine

The condensation products or synthetic resins which

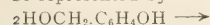
are obtained from the reaction of a solution of formaldehyde, their polymers or equivalents are already well known from scientific and patent literature. The term "phenolic bodies" signifies any substance containing a benzene nucleus and having a hydroxyl attached to the ring, *e. g.*, the cresols

naphthols, thymol, carvacrol, etc., the chlor- and brom-phenols, nitro-phenols, phenol sulfonic acid, etc. The term formaldehyde includes its hydrates or polymers and may be replaced in the reaction by acet-aldehyde, benzaldehyde, etc., in certain cases, but the formaldehyde is in every case more reactive than the substituted aldehyde, or the aldehydes higher in the series.

The formaldehyde-phenol reaction products are formed in every case with the elimination of water as a by-product. The first step in the reaction goes according to the following equation:



forming oxybenzyl alcohol. The second change may be represented by the equation:



in which two molecules of oxybenzyl alcohol unite with the elimination of water and the formation of saligeno-saligenin. Further reaction may occur in which the saligenin molecules unite, forming a saliretin product with the further elimination of water.

The water of reaction is not the only water present, since commercial formaldehyde is 60 per cent water and in the process of formation, this water separates out from the newly formed resin.

The wet process for obtaining the synthetic resins has been exploited successfully, commercially, by a number of research chemists who have patented the results of their researches.

Difficulty is experienced in following the rate of this wet reaction for, heretofore, phenol has been difficult to determine in the presence of formaldehyde and formaldehyde requires a considerable length of time (about 48 hours) for each determination, the results being unreliable within 2 or 3 per cent. Consequently, great difficulty is experienced in following the progress of the condensation.

An attempt has been made by Jablonow<sup>1</sup> to follow the velocity of this reaction in an open system by measuring the rate of change in the specific gravity of the reacting mixtures.

The reaction between a phenolic body and formaldehyde or a polymer is only a part of the more general reaction which takes place between a simple or substituted mobile methylene group and any substance containing in its molecule a benzene nucleus to which a hydroxyl is generally attached.

The hydrogen of the active methylene group may be substituted by the alkyl radicals, giving the higher aldehydes of the fatty series or by a benzene nucleus giving the aromatic aldehydes. The oxygen, to which the active methylene group is attached, in aldehydes, may be replaced by sulfur or nitrogen. With sulfur the malodorous thio-aldehydes are formed; the nitrogen forms with active methylene groups hexamethylene tetramine, hydro-benzamide, etc. The nitrogen compounds are colorless, odorless, transparent and crystalline, easily soluble in water and sparingly soluble in alcohol. They sublime without melting and are stable products; when boiled in dilute acids they break

down into ammonia and the corresponding aldehydes; boiling in alkali has no effect upon them.

Hereafter, the word phenol will be used to designate all compounds having a hydroxyl group attached to the benzene nucleus, and by the term "methylene body" shall be understood all compounds containing an active methylene group; the hydrogen of the group may or may not be replaced by other bodies or radicals and the methylene group may be attached to oxygen, nitrogen, sulfur or their equivalent which allows the methylene to remain active.

#### HISTORICAL

##### Condensation of the Salicylates

As early as 1853 Gerhardt<sup>1</sup> showed that an insoluble resin could be produced by the dehydrating of sodium salicylate by means of phosphorus oxychloride, giving as the reaction  $2(C_7H_5O_3) \longrightarrow C_{14}H_{10}O_8 + H_2O$ . Gerhardt notes that this resin will hydrolyze in KOH solution.

Schroder, Prinzhorn and Kraut<sup>2</sup> in 1869 by dehydrating sodium salicylate with  $POCl_3$  produced a resin insoluble in water, alcohol, ether, etc., which hydrolyzed back in the presence of KOH to salicylic acid. Combustion of the insoluble resin gave:

	Obtained by Socloff	Obtained by Prinzhorn	Calculated for hepta- salicylo- salicylic acid	Calculated for octo- salicylo- salicylic acid	Calculated for nono- salicylo- salicylic acid
C.....	68.94	68.92	68.71	68.85	68.92
H.....	3.64	3.44	3.48	3.46	3.44

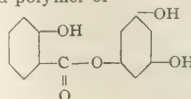
The calculations show for the octo- and nono-salicylosalicylic acid a better agreement with the combustion experiments than does the calculated value for hepta-salicylo-salicylic acid. This larger molecular chain agrees with the results of Beilstein and Seelheim in dehydrating saligenin as recalculated.<sup>3</sup>

The probable linking of the chain is according to the formula



Velden in 1877<sup>4</sup> showed that salicylic acid, in the presence of sodium amalgam and acid, would reduce to an oxybenzylalcohol and then dehydrate into a saliretin body. This same phenomenon has been shown by Dr. Baekeland<sup>5</sup> to be possible when salicylic acid is reduced at the cathode by electrolysis.

Salicylic acid and pyrogallol boiled in absolute alcohol give a product which is soluble in alcohol, has the formula  $(C_{18}H_{22}O_9)$ , and is probably represented<sup>6</sup> by a dehydrated polymer of



##### Condensation of Phenols and Higher Aldehydes

In 1871 Baeyer<sup>7</sup> showed that benzaldehyde and pyrogallol gave a substance insoluble in KOH, the re-

<sup>1</sup> *Ann. der Chemie*, **87**, 159 (1853).

<sup>2</sup> *Ibid.*, **150**, 1 (1869).

<sup>3</sup> Page 5.

<sup>4</sup> *Jahresbericht*, **5**, 37 (1877).

<sup>5</sup> *This Journal*, **4**, 737 (1912).

<sup>6</sup> *Paterno Gazzetta, Chem. Italiana*, **3**, 1 (1872).

<sup>7</sup> *Berichte*, **5**, 25 (1871); **5**, 280 (1872).

<sup>1</sup> *J. Am. Chem. Soc.*, **35**, 811 (1913).

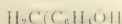
action going according to the equation  $2(C_7H_6O) + 2(C_6H_4O_2) = (C_{28}H_{22}O_7) + H_2O$ . The resin thus produced, reddens on oxidizing and bleaches on reducing, and by heating at  $200^\circ$  C. passes with the loss of hydrogen to a substance of the formula  $C_{28}H_{18}O_7$ .

Phenol and benzaldehyde, with  $H_2SO_4$  as the condensing agent, give a red resin which was soluble with a red color in concentrated sulfuric acid, water, or alkali, and gives, in alkali, a beautiful violet color.

Formaldehyde, phenol and concentrated sulfuric acid give a pasty mass which dissolves in KOH solution.

Trzcinski in 1884<sup>1</sup> working with benzaldehyde and  $\beta$ -naphthol produced a resin which is insoluble in alkalis and which may be represented by  $4C_{10}H_8O \cdot 4C_6H_5 \cdot CHO = (5H_2O)$ .

In 1886 Claus and Trainer<sup>2</sup> showed that aldehydes and ethyl alcohol condensed with HCl gave alkali insoluble products. They showed further that by boiling 2 mols of phenol and 1 mol of acetaldehyde in ether a substance was formed which resembled very closely a higher saliretin in its qualities and gave as its possible formula



$\beta$ -naphthol and acetaldehyde in HCl. gave products insoluble in KOH, while  $\alpha$ -naphthol gave a resin soluble in alkali. Their formula suggested for  $\beta$ -naphthol resin is  $C_2H_4O_2(C_{10}H_7)_2$  and for the  $\alpha$ -naphthol resin  $C_2H_4(C_{10}H_6OH)_2$ .

#### Condensation of Oxybenzyl Alcohols (Saligenin)

Beilstein and Seelheim<sup>3</sup> in 1861 produced a resin from oxybenzylalcohol by dehydrating this substance with acetic anhydride or ethyl iodide which on analysis gave:

	Expt. 1	Expt. 2	Expt. 3	Calculated for $8C_7H_6O_2 \cdot 11H_2O$
C.....	78.02	77.44	77.80	77.59
H.....	5.98	5.93	5.60	5.77

and Kraut<sup>4</sup> in reviewing this work suggests the formula  $C_{68}H_{80}O_9 = 8(C_7H_6O_2) - 7H_2O$  which he names heptasaligeno-saligenin. That would be for a substance where

$$C = 77.59, \quad H = 5.77$$

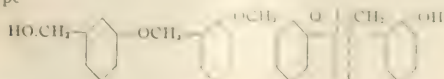
which agrees fairly well with results for Expt. 2; but Expt. 1 agrees better with  $11(C_7H_6O_2) - 10H_2O = C_{77}H_{88}O_{12}$  since for this formula

$$C = 78.02, \quad H = 5.74$$

and Expt. 3 may be represented by  $9(C_7H_6O_2) - 8H_2O = (C_{63}H_{72}O_{10})$  where

$$C = 77.77, \quad H = 5.70$$

From these results, it seems not unreasonable to conclude that the insoluble resin formed is variable and is formed by simply lengthening the molecular chain and may proceed indefinitely. The chain of the type



continuing to grow indefinitely. The longer the chain

the more nearly will the proportions of phenol to the methylene group be 1 : 1.

Moitessier,<sup>1</sup> in 1866, pointed out that saligenin dehydrated and with the loss of one water passed over into a saliretin resin.

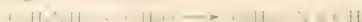
#### Condensation of Benzoic Acids and Formaldehyde

As early as 1871 Baeyer<sup>2</sup> published a monograph on the condensation of phenols with aldehydes in which he concludes "Dass sich alle aldehyde mit allen Phenolen zu Körpern verknüpfen." And Manasse in 1894, working with synthetic resins made from phenols notes that "Es ist keine neue Beobachtung das beide Componenten in Verhältniss 1 : 1 zusammentreten."

Baeyer<sup>2</sup> demonstrated also that formaldehyde could be replaced by chloral or the ammonia aldehydes in water and that the phenols such as pyrogallol, resorcin, benzoic acid, gallic acid, etc., would act similarly to phenol.

Schotten,<sup>4</sup> in 1878, produced resinous substances with formaldehyde and phenols in which the hydrogen of the ring was replaced by such groups as  $-CH_3$ ,  $-NO_2$ ,  $-COOH$ , etc.

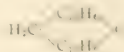
Tollens,<sup>5</sup> in 1874, produced a rather remarkable product from the reaction of formaldehyde on aniline according to the reaction



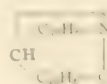
In 1891 Kleeberg<sup>6</sup> made a resin by adding 10 grams phenol to 20 cc. formalin and adding, further, with cooling, concentrated HCl. The result was a resin insoluble in alkali and from this purified resin he could obtain no concordant combustion analysis.

With gallic acid and formaldehyde, a substance  $C_{10}H_{12}O_{10}$  was obtained.

Abel,<sup>7</sup> in 1892, made from  $\alpha$ - and  $\beta$ -naphthol and formaldehyde, in acetic acid, soluble resins which, on treating with alkaline halogens, became quite insoluble going over to the substance



which could be readily reduced with zinc dust in acid solution. Treating the dinaphthol methanes with hydroxylamine produced an insoluble substance



Abel also pointed out that thymol and guaiacol gave condensation products.

In 1892 Hosaeus<sup>8</sup> showed that phenol, resorcin, pyrogallol or phloroglucin heated with dilute formalin in the presence of rather strong  $H_2SO_4$  or HCl gave insoluble resins.

Formaldehyde	1866	1871	1878	1884	1892
Phenol	5	5	5	5	5
Resorcin	5	5	5	5	5
Pyrogallol	11	11	11	11	11
Phloroglucin	17	17	17	17	17
Formaldehyde	263	263	263	263	263
Formaldehyde	25	25	25	25	25
Formaldehyde	25	25	25	25	25

<sup>1</sup> *Berichte*, 17, 499 (1884).

<sup>2</sup> *Ibid.*, 19, 3004 (1886).

<sup>3</sup> B. and S., *Ann. der Chem.*, 117, 8 (1861).

<sup>4</sup> Kraut, *Ibid.*, 186, 123.

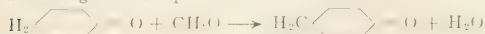


Manasse, 1894, produced a resin by taking

- 1 mol phenol
- 1 mol 40 per cent formalin
- 1 mol caustic soda

and allowing the reaction to take place in the cold; the odor of formaldehyde disappears, and orthoxybenzyl alcohol is the chief product.

Wohl and Mylo,<sup>1</sup> in 1912, working with acrolein suggest the polymerization of formalin and phenol according to the equation



That this does take place to a certain extent may account for the quinone coloring of the resins, being green in alkali, and red in acid.

Lebach<sup>2</sup> (1900-1913) deals, at length, with the application of these resins to specific industries. The resins are produced in every case from the boiling together of phenols and aqueous formaldehyde in the presence of a condensing agent.

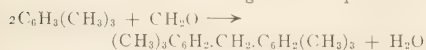
Dr. Baekeland<sup>3</sup> has published a number of original papers on the practical application of these resins which are formed from aldehydes and phenols. A great variety of commercial articles has been produced by the use of these resins as binders, glues, lacquers, varnishes, shellacs, and solid products imitating amber, horn, bone, vulcanized rubber, etc. He showed that this reaction, which is too violent when large quantities of catalysts are added, and too slow as a rule when no catalyst is present, may be controlled effectively by adding less than one-fifth of a formula weight of a basic substance for each mol of phenol present. He pointed out also that the resins formed when a basic substance is present are more insoluble in ordinary solvents than those resins formed in the presence of acids.

Litterschied and Thimme,<sup>4</sup> in 1904, produced insoluble phenolic resins by substituting monochloromethyl ether,  $ClCH_2-O-CH_3$ , for formaldehyde.

#### Condensation of Aromatic Hydrocarbons and Formaldehyde

A very remarkable polymerization<sup>5</sup> takes place when mesitylene (symmetrical trimethylbenzene) is treated with formaldehyde, glacial acetic acid and concentrated sulfuric acid.

The reaction is according to the equation



and this substance is always formed no matter what proportions of the original substances are used.

A similar reaction takes place when benzene and chloral react according to the equation  $C_6H_6 + CCl_3CHO \longrightarrow (C_6H_5)_2HC.CCl_3$ , which yields diphenyl trichloroethane. This remarkable condensation of benzene nuclei with methylenes in the absence of hydroxyls was noted by Baeyer "Es scheinen sich

überhaupt alle Aldehyde unter geeigneten Umständen direkt mit den aromatischen Kohlenwasserstoffen zu verbinden in dessen treten dabei häufig Harze auf."

PATENT LITERATURE.—For fifteen years efforts have been made to commercialize these synthetic phenolic resins. Smith,<sup>1</sup> in 1899, patented a product and process obtained by heating one mol of phenol with 1 mol of formaldehyde and strong HCl, adding wood alcohol and amyl alcohol to retard the reaction. The material was then dried in sheets at 100° C. for 12-30 hours.

Luft,<sup>2</sup> in 1902, in his improved process added such substances as glycerine and camphor to make the synthetic resins more suitable for molding.

Blumer,<sup>3</sup> in the same year, produced a resin suitable as a shellac substitute by using tartaric acid in large amounts as a condensing agent, *e. g.*, 2 mols of phenol, 2 mols of formalin and 1 mol of tartaric acid.

Fayolle,<sup>4</sup> 1903-4, in his French patents uses sulfuric acid as a condensing agent and adds large quantities of glycerine, pitch, oils, etc., as organic fillers.

Story,<sup>5</sup> in 1905, omitted condensing agents altogether; after boiling the phenol and formaldehyde for 8-10 hours at 100° C. the resin is dried out at 80° C.

In 1905 DeLaire<sup>6</sup> introduced caustic as a condensing agent. He used the alkali in equimolecular proportions with the phenol and precipitated the resin from solution by acid.

DeLaire<sup>7</sup> advanced the art further by resinifying phenol alcohols with heat and reduced pressure.

Fried. Bayer & Co.,<sup>8</sup> 1907, patented a process of making odorless shellac substitutes by using *o*-cresol in place of the ordinary phenols.

Helm,<sup>9</sup> 1907, introduced amines and ammonium salts as condensing agents or catalysts. The agents he uses in almost equimolecular proportions.

A series<sup>10</sup> of patents were taken out in 1907 by Knoll & Co. in Germany and by Wetter in Great Britain for H. Lebach in which the condensing agents were acid or alkaline salts; sodium sulfite is specially mentioned. In Brit. Pat. 28,009, 1907, occurs the first mention of the possible use of hexamethylenetetramine. However, the patent text shows clearly that this reaction is no other than a water process, to which a condensing agent has been added.

Grognot,<sup>11</sup> in 1908, patented a process for making phenolic resins in the presence of large quantities of glycerine and after the reaction has proceeded, the desired length distilling off the excess water and glycerine.

Dr. Baekeland<sup>12</sup> has patented processes for pro-

<sup>1</sup> Brit. Pat. 16,247, 1899; Ger. Pat. 112,685, 1899.

<sup>2</sup> Ger. Pat. 140,552, 1902; U. S. Pat. 735,278.

<sup>3</sup> Brit. Pat. 12,880, 1902.

<sup>4</sup> Fr. Pat. 33,584, 1903; 2,414, 1904; 2,485, 1904; 341,043, 1904.

<sup>5</sup> Brit. Pat. 8,875, 1905.

<sup>6</sup> Fr. Pat. 361,539, 1905.

<sup>7</sup> Brit. Pat. 204,811, 1907; Ger. Pat. 189,262, 1905.

<sup>8</sup> Ger. Pat. 201,261, 1907.

<sup>9</sup> Brit. Pat. 25,216, 1907.

<sup>10</sup> Brit. Pat. 28,009, 1907; 24,072, 1908; Swiss Pat. 40,994, 1907; Fr. Pat. 395,657; Belg. Pat. 204,811, 1907.

<sup>11</sup> U. S. Pat. 391,436, 1908.

<sup>12</sup> U. S. Pat. 939,966, 941,605, 942,699, 942,700, 942,808, 942,809, 942,852, 949,671, 954,666, 957,137, 982,230, 1,018,385, 1,019,406, 1,019,407, 1,019,408.

<sup>1</sup> Berichte, 45, 2046 (1912).

<sup>2</sup> Lebach, Zeit. für anorg. Chem., 22, 1598 (1909); Jour. Soc. Chem. Ind., 32, 889 (1913).

<sup>3</sup> Trans. Am. Electrochem. Soc., 15, 149 (1909); THIS JOURNAL, 1, 149, 545 (1909); 3, 932 (1911); 4, 737 (1912); 5, 506 (1913).

<sup>4</sup> Chem. Centr., 1904, Bd. 949.

<sup>5</sup> Baeyer, Berichte, 5, 1091 (1872).



ducing synthetic resins from phenols and formaldehyde in the presence of less than  $\frac{1}{8}$  of a mol of basic condensing agents per mol of phenol. The reaction may be kept well under control if the condensing agent be present in small amounts and the resins are ordinarily more insoluble if basic, rather than acid-condensing agent, be used.

Dr. Baekeland<sup>1</sup> warns against the use of condensing agents in excess of  $\frac{1}{8}$  of a formula weight per mol of phenol for two reasons: (1) the rapid increase in the reaction caused by large amounts of the condensing agent; (2) the trouble which the presence of the condensing agent may cause in the final product; for example, he warns us that "if a large amount of ammonia be used hexamethylene tetramine is formed which is a crystalline body of definite chemical composition." Further "It is therefore essential that the proportion of base should not exceed certain definite limits, and the maximum permissible proportion has been found to be less than  $\frac{1}{8}$  of the equimolecular proportion of the phenolic body present. If larger proportions of base be used, there are formed in the mass, such amounts of disturbing bodies as serve to render the product technically inferior or worthless for the purpose of this invention."

Other patents<sup>1</sup> have been granted recently to Aylsworth in which the resin, resulting from the heating of 2 mols of phenol and one mol of formaldehyde, is hardened by heating in the dry by the addition of a sufficient amount of hexamethylenetetramine.

**PROBLEM.**—From a review, then, of the scientific and patent literature it is evident that there remains to be studied the reaction and the products which are formed when hexamethylene tetramine is made to react in the dry condition with anhydrous phenol. All the previous literature has had to do with phenols and active methylenes in water solution to which condensing agents have generally been added. The quantity and kind of condensing agent has been shown by Dr. Baekeland to be of prime importance in these reactions. Mention of the use of hexamethylene tetramine as a substitute for formaldehyde has been made by Wetter,<sup>2</sup> but it is reasonable to presume, from the context of his patents, that it was to be used in a water solution and in the presence of a condensing agent. All these previous processes require the freeing of the resin from the water contained in the 40 per cent formaldehyde solution and also the water which is a by-product of the reaction. The resins prepared in this way have also to be washed free of the condensing agent.

However, in the case of anhydrous phenol and dry hexamethylenetetramine, there is no water present in the ingredients. Neither is there any water formed as a by-product and no condensing agent is present, which must later be freed from the resins by washing. The only by-product is ammonia and it escapes readily on account of its volatility.

In the study of this anhydrous reaction the conditions are always under exact control and the reactions are definite and easily followed. The resins formed

have very great commercial possibilities on account of their uniformity, chemical inertness, dielectric properties, mechanical strength, high refractive index (lustre), plasticity at certain stages and the cheapness and supply of the raw materials from which these resins are manufactured.

#### THE REACTION BETWEEN HEXAMETHYLENETETRAMINE AND PHENOL

##### *Hexamethylenetetramine Triphenol*

The simplest product which forms when phenol reacts with hexamethylenetetramine is the addition product hexamethylenetetraminetriphenol<sup>1</sup> which crystallizes out of a cold water solution.

Lebach,<sup>2</sup> 1909, states that hexamethylenetetramine triphenol when heated by itself, i. e., in the dry, goes over with the evolution of ammonia into "einen gelben unlöslichen und unschmelzbaren Körper über, der nichts anderes ist als Bakelit." The reason for this conclusion doubtless lies in the fact that the insoluble material has the same yellow, transparent, glossy appearance as Bakelite which has been made from phenol and formaldehyde using ammonia as the condensing agent. However this may be, the material has not at all the same composition as Bakelite. Dr. Baekeland gives as his conclusion from his experiments that Bakelite consists of a material in which 6 phenols<sup>3</sup> have united with 7 methylene groups.

Hexamethylenetetraminetriphenol has a composition of 6 phenols for every 12 methylenes, or 41.7 per cent more methylene than is necessary for making Bakelite.

Another argument which must be brought in opposition to this conclusion lies in the fact that Dr. Baekeland represents the addition of the seventh formaldehyde group directly to the molecule without the elimination of the oxygen in the formaldehyde as shown in the equation<sup>4</sup> with the elimination of water. Now in the dry this final reaction can not possibly take place. No oxygen or water is present to form with the methylene group, formaldehyde. Indeed the only oxygen present in the reaction is contained in the hydroxyl of the phenol and as we have shown in the case of anisol and phenetol<sup>5</sup> when the hydroxyl group becomes inactive no reaction takes place between hexamethylenetetramine and the compound containing the benzene nucleus, it seems reasonable, therefore, to assume that the oxygen of the hydroxyl is not interfered with as this reaction proceeds normally and produces the insoluble resin. We have shown elsewhere<sup>6</sup> that in the reaction between phenol and hexamethylenetetramine no water is evolved.

When hexamethylenetetraminetriphenol is heated, there escapes not only ammonia and a small amount of phenol but also there is present a strong fishlike or mouse odor of methylamines. The latter by-product is not present when the phenol is increased to 6 mols of phenol to 7 methylenes. Such a resin with

<sup>1</sup> U. S. Pat. 941,800 (1909).  
<sup>2</sup> U. S. Pat. 1,000,000 (1911).  
<sup>3</sup> Loc. cit.  
<sup>4</sup> U. S. Pat. 1,000,000 (1911).  
<sup>5</sup> U. S. Pat. 1,000,000 (1911).  
<sup>6</sup> U. S. Pat. 1,000,000 (1911).

twice the amount of necessary methylene would be not only costly but useless both in the quality of the resin and the offensive methylamine odor which it possesses.

With the formation of different by-products, the absence of water or oxygen to form methyleneglycol or formaldehyde, thereby preventing the hardening process from taking place according to Dr. Baekeland's formula and the proportions of phenol to methylenes being 6 : 12 instead of 6 : 7 it seems untenable to hold that the yellow material which forms when hexamethylenetetramine triphenol is heated in the dry, is Bakelite.

The resin aggregate resulting from the heating of dry hexamethylenetetramine triphenol at 175° C. or higher for 1 hour, with the evolution of ammonia and methylamines will swell, soften and partly dissolve or disintegrate in boiling phenol with a strong evolution of ammonia. This indicates the very evident fact that hexamethylenetetramine or some of its degradation products are present in some form in the resin. A further proof of this lies in the fact that the aggregate swells in dilute HCl. No other resin which we have made swells in acid. All other resins, even the alcohol-soluble "Novolak" remains quite unaffected in an acid solution. The swelling indicates that there is present in the aggregate a material which is soluble in acid.

In the wet process it is impossible to say that the substance which is reacting in solution to produce the resin is hexamethylenetetramine triphenol. There are no methylamines given off as by-products and the excess hexamethylenetetramine remains in the water solution while the resin which forms has a ratio of phenol to methylene 13 : 12 in the early stages of heating and the final product has a ratio of 6 : 6.

#### Hexamethylenetetramine and Phenol (Wet Process)

When 1 mol of hexamethylenetetramine and 6 mols of phenol are dissolved in 500 cc. of water and the solution boiled, a light yellow colored, transparent, amber-like, viscous liquid begins to separate out which on continued heating becomes very viscous and finally changes to a brittle amber solid when cold. This reaction is probably identical with that which takes place when 1 mol of formaldehyde and 1 mol of phenol are heated together, using ammonia as a condensing agent to hasten the reaction.

The general conditions have been presented which occur when an active methylene group reacts with a phenolic body in the presence of water. A very different set of reactions takes place when no water is present during the reaction.

#### By-products of the Dry Reaction

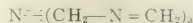
When formaldehyde is used the by-product formed is water, the reaction taking place with the dehydration of the product as follows:



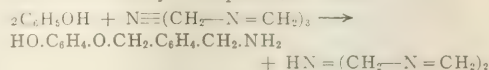
The reaction continues with increasing size of the molecule and further elimination of water.

If, however, dry hexamethylenetetramine and an-

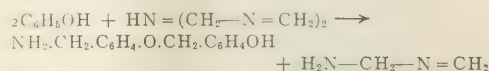
hydrous phenol be mixed together and the mixture heated at 60° C. or higher a reaction begins with the evolution of ammonia, and ammonia is the only by-product as shall be shown later. If the phenol be present in excess, and if the mass be heated to the boiling point, the reaction is very rapid. Practically all the ammonia is given off in the first ten minutes of the boiling and the reaction is quite complete and all the nitrogen has been evolved as ammonia within 2 hours from the beginning of the reaction. The reaction takes place probably in a series of steps. Accepting the formula of hexamethylenetetramine as



this reaction may take place as follows:



and a second reaction may occur



This process continues until all the CH<sub>2</sub> groups have combined with the phenol and ammonia remains as the by-product. The intermediate product, amino-saligeno-saligenin, has been isolated and will be described in a later paper. No nitrogen and no methylamines are given off in measurable quantities at any stage in the process. No water is formed<sup>1</sup> and the nitrogen contained in the hexamethylenetetramine is evolved quantitatively as ammonia as will be shown later.<sup>2</sup> This reaction between a phenolic body and an active methylene group may be followed by simply measuring the amount of ammonia which has been evolved. This is especially true if the phenol is in excess, e. g., if 24 mols of phenol be heated with 2 mols of hexamethylenetetramine the final product is a resin in which the methylene groups have united with the phenols in the ratio of 13 phenols to 12 methylenes.<sup>3</sup> The remaining 11 mols of phenols are present as free phenol and may be separated easily from the resin by dissolving the mass in dilute sodium hydroxide after the ammonia has all been evolved, neutralizing the solution or making it acid with HCl and filtering off the precipitated resin.

#### THE RESINS IN EXCESS PHENOL

The resin which forms when hexamethylenetetramine is heated in the presence of excess anhydrous phenol seems always to be the same material and resembles very closely Novolak.<sup>4</sup> It is soluble in alcohol, acetone, phenol, caustic, etc., and is insoluble and precipitated from its solution by acids. Heated, it does not harden rapidly but remains a liquid at high temperatures melting at 105-110° C. and remaining liquid at 180° C. for many hours. If the heating is continued, a flexible dark red skin forms over the surface which is only partly soluble in alcohol. A

<sup>1</sup> Baekeland, THIS JOURNAL, 3, 932 (1911); 4, 741 (1912).

<sup>2</sup> See pages 11 and 12.

<sup>3</sup> See page 11.

<sup>4</sup> See analysis of Novolak, page 10.

peculiar gas is given off during the heating which has the odor of burning phenol. When cold the resin hardens to a glossy material which is more brittle than common rosin and apparently quite useless as a commercial product. This resin is not a solution of the final product in phenol but is an individual having definite chemical properties and heating does not readily polymerize it.

A variation in the amount of excess phenol present does not alter the characteristics or the amount of the synthetic resins formed when a definite amount of hexamethylenetetramine is used; *e. g.*, if 18 mols of phenol and 1 mol of hexamethylenetetramine be heated until the ammonia has ceased to evolve, the same amount of resin is formed and the resin has the same characteristics as when 12 mols of phenol are heated with 1 mol of hexamethylenetetramine until ammonia ceases to evolve.

As the amount of excess phenol is gradually decreased the mass which is left in the flask after the ammonia has ceased to come off changes its physical properties, for all combinations of phenol with hexamethylenetetramine; those above 12 mols of phenol to one mol of hexamethylenetetramine remain a yellow liquid whether hot or cold and are in reality a solution composed of the soluble resin described above and the unused phenol. But as the phenol is decreased below the ratio of 12 mols of phenol to 1 mol of hexamethylenetetramine, the liquid thickens and finally, as the excess of free phenol decreases, the resin changes to an infusible insoluble transparent yellow or red solid at all temperatures. Nine mols of phenol to 1 mol of hexamethylenetetramine give an aggregate which is quite solid and brittle in the cold and a tacky rubbery mass when hot ( $170^{\circ}\text{C}.$ ). Eight mols of phenol to one of hexamethylenetetramine give a mass which is solid at all temperatures, not as brittle in the cold as the 9 : 1 resin but rubbery when hot, like polymerized tung oil. The more the phenol is reduced the less elastic and resilient the mass becomes when hot and at the ratio of (5.00-6.5) mols of phenol to one mol of hexamethylenetetramine the material is quite solid and hard at all temperatures; at room temperatures it is a solid which is not brittle but hard, dense, transparent and tough, with a tensile strength ranging from 4,000-5,200 lbs. per sq. inch. When hot it can be bent about like a hard filled rubber. Decreasing the phenol below 5.3-6.5 mols to one hexamethylenetetramine again increases the brittleness of the resin due to the excess of the crystalline hexamethylenetetramine. The product, however, does not melt at any temperature.

#### RESIN FORMED

Statements have been made to the effect that the addition of the proper amount of hexamethylenetetramine to phenols or phenolic resins to form a 6 : 1 resin produces a brittle or exceedingly rigid evolution of ammonia and leaves a very porous, dry mass. This is true in some of limited cases. The rate of the evolution of ammonia may or may not be rapid, depending upon the method of carrying out the experiment. It is true in a water bath at  $100^{\circ}\text{C}.$

for 25 hours, less than 50 per cent of the total ammonia will be evolved and the mass is a viscous liquid when hot, and a brittle solid when cold.

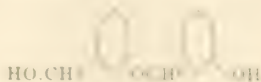
On the other hand, if a 6 : 1 mixture is heated rapidly at  $180^{\circ}\text{C}.$  a spongy material soon forms which may have a volume twenty times that of the original materials. This porous form of the resin is very advantageous when the material is to be pulverized later, since it powders in the ball mill in less than one-tenth the time required to pulverize solid lumps of the resin.

This finely ground material, when pressed in hot molds under a pressure of 4-6 tons to the sq. in., becomes a homogeneous, transparent, solid of maximum mechanical strength, highest dielectric properties, and chemical inertness.

The grinding and molding of the powdered material in hot molds, under pressure, is only one of a number of methods which we have in use in this laboratory for producing transparent solid goods. By a simple manipulation of the material, during heating, it is possible to produce large pieces of the final transparent, insoluble resin without the use of external pressure. We have, at present, in our laboratory rods of this material 2 feet long and  $1\frac{1}{2}$  inches in diameter which have been produced by simply pouring the material while liquid into open molds and allowing it to harden under suitable heat treatment *without the application of external pressure*. These rods in the final condition are homogeneous, almost water white transparent and free from fractures or gas bubbles.

#### INTERMEDIATE AND BY-PRODUCTS

It might at first be supposed that some oxybenzyl alcohols or substituted saligenin would be present at the end of the reaction. This of course, is impossible when it is remembered that no water is present and all the ammonia has been evolved; oxybenzyl alcohol, saligeno-saligenin, oxybenzylamine or an amid saligenin are also impossible since there is present in the remaining mass no water or oxygen necessary to form the alcohols and no nitrogen remains to form the corresponding amines. Such a compound, therefore,



which is probably the second product formed when phenol and formaldehyde react, is impossible when phenol unites with hexamethylenetetramine in the dry. The intermediate products which form may be  $\text{NH}_2\text{CH}_2\text{C}_6\text{H}_4\text{OH}$ ,  $\text{NH}_2\text{CH}_2\text{C}_6\text{H}_4\text{OCH}_2\text{C}_6\text{H}_4\text{OH}$ ,  $\text{C}_6\text{H}_4\text{OCH}_2\text{C}_6\text{H}_4\text{OH}$ , etc., but at the end of the reaction the first two products can not be present as all the nitrogen present in the hexamethylenetetramine has been evolved as ammonia. And as we shall now show the final product which forms in *excess phenol* is a definite compound. This compound has little or no tendency to polymerize or harden and being insoluble in boiling water when mixed with



active methylene compounds transforms readily into the infusible resins.

### Combustion Analysis of the End Product Formed in Excess Phenol

The analysis of a resin which we have prepared by boiling a mixture of 12 mols of dry phenol and 1 mol of hexamethylenetetramine until all the nitrogen has been evolved as ammonia, dissolving the resulting thick, yellow liquid in 5 per cent KOH and precipitating with 2*N* HCl, the precipitate filtered off into Norton cones and washed with 2*N* HCl and dried at 50° C. in a gas oven gave results as follows:

Calculated for $C_{104}H_{82}O_{16}$	Found	Calculated for $C_{90}H_{80}O_{14}$
C = 78.16%	C = 77.98%, 77.96%	C = 78.04%
H = 5.81	H = 6.17, 6.23	H = 5.88
O = 16.03	O = 15.85, 15.81	O = 16.16

(1)  $C_{104}H_{82}O_{16}$  may be written  $14(C_6H_5O)_2C_6H_4O_2H_2O$

(2)  $C_{90}H_{80}O_{14}$  may be written  $12(C_6H_5O)_2C_6H_4O_2H_2O$  or  $C_6H_5OCH_2C_6H_4OCH_2C_6H_4OCH_2CH_2OH$

Dr. Baekeland's published analyses of certain soluble products which he has obtained by heating excess phenol in the presence of formaldehyde solution<sup>1</sup> and by heating oxybenzyl alcohol and phenol are as follows:

Calculated for $C_{104}H_{82}O_{16}$	Found for Phenol + $CH_2O$	Found for Saligenin + Phenol
C = 78.16%	78.04% 77.95%	78.16% 78.24%
H = 5.81	5.79 5.97	5.65 5.75
O = 16.03	16.17 16.08	16.19 16.01

That the end of the molecular chain in the individual, made as described above, can not have a  $-CH_2OH$  group attached to the benzene ring is evident from the fact that the reaction between anhydrous phenol and hexamethylenetetramine could not produce such a substance, especially since, as will be shown presently, the only by-product from the reaction is ammonia. The other end of the molecule is hydroxylated, probably, as the substance is readily soluble in alkalis.

The  $H_2O$  may be either a hydration which attached itself to the molecule during the process of solution and precipitation, or, which seems more reasonable, the process is one of oxidation, for the individual changes its color from yellow to green when it dissolves in alkali and from green to red when it is precipitated by acid. The drying of the pptd material at 50° C. changes the color further to a reddish brown. This possible oxidation is described at further length on page 14. Such a formula would have a molecular weight for  $C_{104}H_{82}O_{16} = 1552$  or for  $C_{90}H_{80}O_{14} = 1384$ . The highest formula weight calculated from the rise in boiling point which Dr. Baekeland<sup>2</sup> has found for novolak dissolved in acetic acid is 1216.

Aylesworth<sup>3</sup> in his U. S. patent 1,029,737 lays claim to the production of a soluble phenolic resin formed from phenol and formaldehyde by boiling 2 mols of phenol in 1 mol of aqueous formaldehyde until a resin is produced having the formula  $C_6H_5OCH_2-$

$C_6H_4OCH_2C_6H_4OH$  as shown by boiling-point analysis. This is quite impossible for the reason that such a resin is not an individual but may be dissolved up in KOH and separated into two constituents by the addition of HCl, the precipitate containing approximately 50 per cent and the filtrate holding in solution approximately 50 per cent of the original phenol used. The rise in the boiling point given by Aylesworth is no doubt caused by the 50 per cent free phenol and shows that the molecule of the resin is so large in the precipitate as to have very little effect upon the boiling point of the solvent employed as the rise in the boiling point may be accounted for by the free phenol present.

A further proof that the molecule consisting of 12 methylenes and 13 phenols is from the fact that the total amount of resin formed in a phenol solution, and which is precipitated by the acid as described above, corresponds in weight to  $6\frac{1}{2}$  phenols to each 6 methylenes added or 13 phenols to 12 methylenes. This is in agreement with the combustion analysis, and with the highest number obtained in the rise of boiling points. The formula then which we propose for this soluble resin is  $C_6H_5OCH_2(C_6H_4OCH_2)_{11}.C_6H_4OH$  and following Kraut's<sup>2</sup> suggested nomenclature we have called this material phenyl-endecka-saligeno-saligenin.

That this resin is an intermediate product which later is transformed by being mixed with formaldehyde or hexamethylenetetramine and heated into the insoluble infusible methylene-phenol condensation products of the highest dielectric and tensile strength and chemical inertness, is almost certain from the fact that an aggregate can be made consisting of 10 mols of phenol to 1 mol of hexamethylenetetramine and this heated until all the ammonia has been evolved which results in a heavy, viscous yellow transparent liquid when hot and semi-solid when cold, consisting of over 63 per cent phenyl-endecka-saligeno-saligenin (novolak), the rest being water-soluble phenols; hexamethylenetetramine is then added in such proportions as to make the total phenol to methylene in the ratio of 1 : 1 and heated until the mass has become a yellow porous sponge, the mass is then powdered and pressed in molds at 200° C. and 12,000 lbs. per sq. in. for 5-10 mins. and the resin becomes a transparent amber-like material with a dielectric strength of 50-90,000 volts per mm., an ohmic resistance of  $2 \times 10^8$  per  $cm^2$  and a tensile strength of 4000-4500 lbs. per sq. inch.

That a substance consisting of more than 60 per cent phenyl-endecka-saligeno-saligenin and the remainder a water-soluble phenol is transformed by the addition of hexamethylenetetramine and further heating into an insoluble substance of such high dielectric and tensile strength seems to preclude the possibility of this resin remaining unchanged or transforming into any other product than an insoluble infusible resin of highest dielectric and tensile strength. For it must be remembered that this resin, of itself, is more brittle than cheap rosin and soluble in all the ordinary solvents.

<sup>1</sup> L. H. Baekeland, THIS JOURNAL, 1, 545 (1909).

<sup>2</sup> THIS JOURNAL, 1, 545 (1909).

<sup>3</sup> I. W. Aylesworth, Brit. Pat. 4,396, 1911.

<sup>1</sup> H. Lebach, Jour. Soc. Chem. Ind., 32, 561 (1913).

<sup>2</sup> Ann. der Chemie, 166, 123.

Indeed we have found this intermediate substance present in all the materials we have made of whatever variety, soluble or insoluble, whether heated for a long or short period and whether at a high or relatively low temperature. Low temperature, a short time of heating and excess phenol or what is the same thing, not enough hexamethylenetetramine to make a 6 mols of phenol to 1 mol of hexamethylenetetramine resin gives a greater percentage of this soluble resin. It is also present in small proportions in 6:1 resins that have been heated for many hours at 200° C.

The following table gives the result of a few analyses of resins as described:

RESIN AND HOW MADE	Weight of phenol used	Weight of hexamethylenetetramine used	Weight of product	Percent soluble resin
Dry phenol and hexamethylenetetramine heated on a water bath 24 hrs., later, heated in an air bath at 100° C. for 24 hrs.	5.8	0.8	7.2	75.0
A Bakelite pipe item bought in the market	5.8	0.8	7.2	75.0
Bakelite lacquer No. 8 satin finish	5.8	0.8	7.2	75.0
6:1 resin heated 18 hrs. at 125° C.	6.0	1.0	7.0	85.7
6:1 resin, containing 2 per cent naphthalene, heated 10 hrs. at 125° C.	6.0	1.0	7.0	85.7
6:1 resin heated later in mold for 1 hr.	6.0	1.0	7.0	85.7
6:1 resin heated for 8 hrs. at 185° C.	6.0	1.0	7.0	85.7

(a) The lacquer was 22 per cent resin and 78 per cent solvent. The percentages in the table are calculated on the resin.

(b) This is doubtful as the figure was obtained by the residual bromination method and the results calculated for free phenol. The real values are probably higher.

(c) 6:1 resin formed by heating together 6 mols of phenol and 1 mol of hexamethylenetetramine.

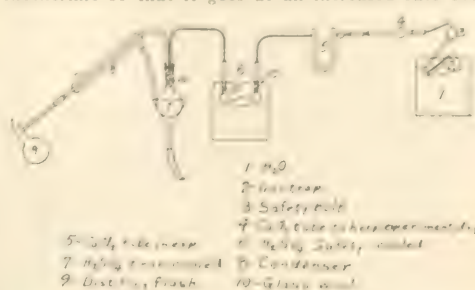
When the soluble, brittle, fusible resin is mixed, powdered and heated for 1 hour with hexamethylenetetramine in the proportions of 6 mols of novolak to 1 mol of hexamethylenetetramine, assuming one mol of novolak,  $C_{10}H_{10}O_4 = 1.54$  times the mass, becomes largely insoluble in all ordinary solvents, caustic alkalis, etc. It swells or gelatinizes in boiling phenol but does not dissolve and exhibits generally the properties of the insoluble products. The final resin formed from the novolak and hexamethylenetetramine is much darker than the resin formed directly from phenol and hexamethylenetetramine. This is, no doubt, due to darkening which takes place when the resin is separated from the excess free phenol.

#### By-Products Formed in the Reaction Between Anhydrous Phenol and Dry Hexamethylenetetramine

An apparatus was arranged as shown in the accompanying diagram. A flame with a long delivery tube was sealed off after the hexamethylenetetramine and phenol were added. The delivery tube led into a reflux condenser, thence into a safety trap, sulfuric acid Marchand U-tubes and finally through a  $CaCl_2$  tube and safety bulb into a gas trap over water.

These experimental results were obtained by the courtesy of Mr. Weston Carpenter.

The flask containing the hexamethylenetetramine and phenol was then heated carefully. Great care was necessary as the reaction is rapid, being strongly exothermic so that it goes at an increased rate even



after the flame is removed if the initial heating has not been sufficiently slow to allow the first of the reaction to take place at a moderate rate until the ammonia has been partly evolved. Checks were kept upon the reaction in four ways:

- (1) The loss in weight in the flask.
- (2) The increase in weight in the Marchand tubes.
- (3) Titration of the ammonia which came over by boiling it off from the  $(NH_4)_2SO_4$  on the addition of KOH.
- (4) Direct titration of the ammonia in duplicate experiments.

The following table shows the result of three experiments:

Experiment	Weight of phenol used	Weight of hexamethylenetetramine used	Weight of product	Percent soluble resin
1	5.8	0.8	7.2	75.0
2	5.8	0.8	7.2	75.0
3	5.8	0.8	7.2	75.0

The results show that the loss in the flask agrees very closely with the calculated yield of ammonia from the hexamethylenetetramine used. The titration of the ammonia here, as in many other experiments, has practically always been 100 per cent of the nitrogen present and the gain in the concentrated sulfuric acid just equals the amount of  $H_2O$  and agrees also with the loss from the flask.

Care was taken to include, in the final weight of the flask, the weight of phenol found in the washings from the reflux condenser and the trap. This generally amounted to less than 0.05 gram of phenol.

To prevent the escape of any ammonia in the rubber joints the glass tubes were placed end to end, over which was drawn very thick walled rubber tubing which previously had been given a heavy coat of pyroxylin varnish.

In the Marchand U-tubes some care was needed to prevent the sulfuric acid from splashing as the ammonia absorbed rapidly and the sulfuric acid struck back. This was overcome by absorbing part of the ammonia in a small amount of sulfuric acid in the first tube and the remainder of the ammonia in the



second tube. Glass wool plugs prevented the splashing and the results are fairly concordant. Simple as the reaction would seem to be, the very rapid evolution of the ammonia in the early part of the experiment made a number of experiments necessary before the present apparatus was devised and the ammonia could be absorbed in its rapid evolution without allowing any of it to escape.

We concluded then from these experiments that no water is formed in the reaction or it would be evolved during the boiling which takes place at  $180^{\circ}\text{C}$ . for two hours and the loss in the flask would not equal the calculated loss for ammonia and the actual weight of ammonia found by titration and by weighing as  $(\text{NH}_4)_2\text{SO}_4$ . It was not considered sufficient to simply weigh the ammonia coming off, as methylamines if present would increase the weight and give useless results. Nor was the titration alone sufficient as it did not distinguish between ammonia and methylamines. The two experiments were necessary in order to check up the results and to make certain that no other product than  $\text{NH}_3$  is evolved during this reaction between phenol and hexamethylenetetramine. The resin which formed in the flask was the soluble, fusible phenyl-endeke-saligeno-saligenin dissolved in the excess phenol.

#### THE ACTIVE HYDROGEN ON THE BENZENE NUCLEUS

The hydrogen which is replaced in the ring is apparently very largely the ortho-hydrogen although either the meta- or the para-hydrogen may possibly be replaced. This reaction is similar to the formation of orthoxybenzylalcohol when phenol and formaldehyde are treated in the presence of  $\text{NaOH}$ .

To test this statement, three experiments were undertaken with the cresols: 5.1 grams of each of the pure cresols were weighed out separately into test tubes and to each 1.1 grams of hexamethylenetetramine were added. The three test tubes were placed in a thin beaker which rested on a block of wood, in an electric oven at  $135^{\circ}\text{C}$ . In a few minutes the meta-cresol began to react giving off ammonia and passing over into an insoluble, yellow, scoriaceous resin which, when hot, was rubbery for a very short time, but soon transformed into a hard non-rubbery resin at  $135^{\circ}\text{C}$ .

The para-cresol acted in the same way as did the meta-cresol although slightly slower. The two resins were identical in appearance and general properties.

The ortho-cresol acted very differently. After three days of heating the reaction had proceeded only far enough that the mass was a viscous, yellow liquid when hot ( $135^{\circ}\text{C}$ .) and a brittle solid when cold. The reaction was very slow and did not evolve ammonia rapidly at any time. When heated at  $200^{\circ}\text{C}$ . for 30 minutes it formed into a rubbery, resinous mass when hot and a hard rather brittle solid when cold.

On the whole, then, the para- and meta-cresols acted rapidly and similarly while the ortho-cresol acted very slowly and did not form a resin which when hot was hard and solid.

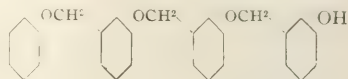
This delayed reaction of the ortho-cresol may be explained as a steric hindrance for the hydroxyl.

It may also be explained as due to a substitution

of  $1/2$  the active (ortho) hydrogen in the ring by a non-reactive group. The latter seems the more probable. The fact that the meta- and para-cresols are very rapid in reaction seems to indicate that the meta- and para-hydrogens are not the ones which are replaced during the formation of the synthetic resin.

#### THE ACTIVITY OF THE HYDROGEN IN THE HYDROXYL GROUP

Of the proposed formula for these condensation products, the more reasonable seems to be the straight chain formula with the phenol rings linked together with the  $-\text{CH}_2\text{O}-$  group in between, the attachment being made at the hydroxyl of the phenol and at the ortho hydrogen of the ring as follows:



The reason for assuming that the reaction is closely connected with the hydroxyl group lies in the fact that if the hydrogen of the hydroxyl or the hydroxyl itself be replaced by a non-reactive group, no apparent reaction takes place after prolonged heating either in the dry or in wet processes. For example, if anisole be heated at the boiling point with hexamethylenetetramine in the absence of water for one week continuously, no appreciable reaction takes place. The anisole remains a colorless, transparent, mobile liquid with the anisole odor and the hexamethylenetetramine settles out on cooling as a crystalline salt. The salt was tinged slightly yellow but further than that no reaction was noticeable.

If the hydroxyl be replaced by hydrogen, *e. g.*, if naphthol be replaced by naphthalene, no reaction takes place after prolonged heating in the dry or wet while with  $\beta$ -naphthol in the absence of water the reaction is very rapid.

#### THE REPLACEMENT OF THE HYDROXYLS IN THE RESINS BY NON-REACTIVE GROUPS

The fact that phenol-formalin resins, made up into lacquers and heated in thin films insoluble in alcohol, acetone, etc., are attacked slowly by caustic potash leads one to the conclusion that whatever substance is formed it very probably contains a percentage of free hydroxyl. So long as the hydroxyls are present it is to be expected that the substance remains at least partly or slowly soluble in free caustic.

Working upon the assumption that the reaction continues as an open chain of benzene rings linked together by the group  $-\text{O}-\text{CH}_2-$  which does not finally form a closed ring or an inner anhydride, it was desirable to fill the hydroxyl on the end of the long chain with an inert group, or to replace the hydroxyl entirely.

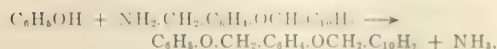
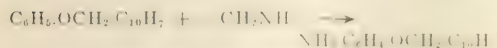
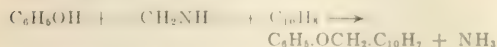
The similarity of anisole and phenetol to phenol and the inertness of their alkylated hydroxyls suggested their use in small quantities in making caustic insoluble resins.

A resin was made up consisting of 6 mols phenol, 1 mol anisole and 1 mol hexamethylenetetramine. The

mixture was heated for a short time in an open beaker and cooled while still liquid. The resin was a light, transparent, amber-yellow color, solid at ordinary temperatures and soluble in alcohol and acetone although more slowly soluble than the ordinary resins made up without the addition of anisol.

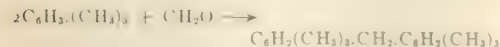
When made into a lacquer and cooked at 170° C. on brass sheets it gave a light transparent film which was insoluble in acids, alcohol, acetone and *N* caustic potash. It required 72 hours to loosen the film with the caustic. All lacquer films from resins made of phenol and an active methylene, whether made in the presence or absence of water with or without the ordinary condensing agents, are attacked by *N* caustic within 24 hours, the lacquer coating reddening in a short time after the caustic is added. The film from resins compounded of 6 mols of phenol and 1 mol of anisol or phenetol remained unreddened and quite unattacked by the *N* caustic potash at the end of the first 24 hours and at the end of 72 hours was only slightly attacked along the edges of the coated brass strips and at no time was any reddening of the lacquer film noticeable.

The explanation for this increased insolubility of the resin and of its greater resistance to color changes seems to lie in the absence of free hydroxyl. This is best illustrated for naphthalene from the following equations:



etc.

and this reaction may continue indefinitely. This resin would no longer have the properties of a substance possessing free hydroxyls, but it would display the inert characteristic of an ether-like anisol which is not broken down in the presence of boiling caustic potash. That such a reaction is possible may be inferred from Baeyer's<sup>1</sup> work with mesitylene and formaldehyde giving, according to the equation,

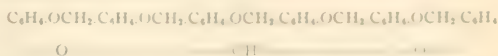


If the hydrogen in a mesitylene ring is active in the presence of  $\text{CH}_3\text{O}$  and forms water with the oxygen of the formaldehyde leaving a substance formed by dehydration behind, it is not unreasonable to assume that at high temperatures ( $180^\circ \text{C.}$ ) a hydrogen on the naphthalene ring may be sufficiently active to form ammonia with an amino group, and leave a resin as a by-product which has no free hydroxyl at the end of the molecular chain as described above. The permanence in the yellow color of the resin or lacquer and their insolubility in normal caustic, as well as all other ordinary solvents, point to the absence of free hydroxyls in the substance.

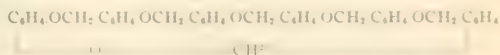
THE RIVAL PRODUCTS OF THE INSOLUBLE INFUSIBLE  
RUBBERS

The transformation of the phenyl-endeke-saligeno-saligenin into the final, insoluble, infusible resin is brought about by the further condensation of its molecules by active methylenes.

Dr. Baekeland concludes that the final product is not obtained through the polymerization of novolak as an intermediate product, but that the growth of the chain stops when six phenols have entered and that an extra hydrated formaldehyde forms with the six phenol chain an inner anhydride as shown by the following formula:



This inner anhydride, he assumes, polymerizes into the insoluble, infusible resin. That this can not be the mechanism of the reaction in the case of the production of these synthetic resins by means of anhydrous hexamethylenetetramine, is evident from the fact that no water or oxygen is present which could possibly form such an inner anhydride as above described. If the reaction takes place with the formation of the larger ring it would be according to the formula



and would lack at least one oxygen in the molecule which the inner anhydride formula requires. This oxygen might, in certain cases, be replaced by nitrogen although this is improbable as the final product never yields more than a trace of nitrogen and even this amount may be mechanically locked as ammonia in the final product.

Further it may be mentioned that the larger molecule of phenyl-undeca-saligeno-saligenin, *i. e.*, 13 moles of phenols : 12 moles of methylenes, could not, without hydrolyzing into a shorter chain, yield such a molecule as Dr. Baekeland proposes.

Recently, Dr. Raschig<sup>1</sup> has proposed certain formulas for the condensation of phenols and active methylenes which, apparently, are not identical with any of the substances isolated as products of this reaction. His formulas show that in passing from "Bakelite I" to "II" the carbon content increases from 77 per cent to 81.4 per cent while in actual results all the combustion analyses of Bakelite which Dr. Baekeland has published and the analyses which we have carried out of these synthetic resins, show that the carbon content decreases from 78.1 per cent to 79 per cent or lower as the resins pass from the soluble to the insoluble state. As these proposed formulas evidently do not agree with actual analyses they will not be considered further.

In arriving at an empirical formula for the final resin, a series of combustion analyses were carried out on products prepared as described in the following table:

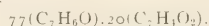
## PREPARATION OF RESIN

	C	H
The insoluble material from a resin hardened with formaldehyde and washed free of substances soluble in normal NaOH.....	75.58	6.08
	75.34	6.11
A 6:1 resin containing traces of anilol heated in air at 175° C. for 6 hours then pressed in a mold at 12,000 lbs. pressure in for 5 min. at 200° C.	74.56	6.40
	75.01	4.50
	74.74	6.35
	75.32	6.55
	75.02	6.35
6:1 resins heated at 200° C. for 100 hrs.....	78.83(a)	5.47
	75.58	5.20

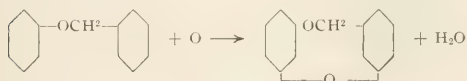
(a) Unaccountably high.

The average of the eight analyses gives C = 75.4  
H = 5.9  
O = 18.7

which corresponds to



The group  $C_7H_4O_2$  may be explained as an oxidation in which 2 hydrogens are replaced by an oxygen somewhat as follows:



Simultaneous with this oxidation is a reddening which takes place rapidly at increased temperatures, *i. e.*, above 200° C. The oxidation probably reaches an equilibrium at  $49(C_7H_6O).48(C_7H_4O_2)$ .

*Reasons for Accepting the Chain Formula*

Oxybenzyl<sup>1</sup> alcohol condenses by dehydration to a resin which yields, on combustion analyses, an empirical formula represented by  $8(C_7H_8O_2) - 7H_2O$  or  $11(C_7H_8O_2) - 10H_2O$ . This condensation is most easily represented by the chain constitution,

$\text{HOCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{O.C}_6\text{H}_4\text{CH}_2\text{O} \dots \text{C}_6\text{H}_4\text{OH}$ , and since the resin is soluble in caustic potash the hydroxyls are free as the formula indicates and not an inner anhydride. The close resemblance of the phenol-methylene condensation to the condensation of oxybenzyl alcohol is apparent.

The salicylate<sup>2</sup> condensations which are closely allied to the dehydration of oxybenzyl alcohol pass, with the loss of water, to a resin represented by  $9(C_6H_4OH.COOH) - 8H_2O$  which is most easily represented by a chain formula,



This resin not only dissolves in a solution of KOH but is hydrolyzed by it back into salicylic acid.

The fact that the soluble resin which we have named phenyl-undeka-saligeno-saligenin and which is similar to the resin which Dr. Baekeland calls novolak and which we have shown to possess the probable formula  $\text{C}_6\text{H}_5(\text{OCH}_2\text{C}_6\text{H}_4)_{11}\text{OCH}_2\text{C}_6\text{H}_4\text{OH}$  passes with the further absorption of methylenes to the insoluble resin, is the strongest argument in favor of the material being a chain molecule of indefinite length. If the resin novolak passes to the insoluble resin of greatest chemical inertness, tensile strength, etc., as we

have ample proof that it does, then so large a molecule as novolak could not possibly pass to the final inner anhydride formula which Dr. Baekeland suggests for Bakelite C, unless the larger molecule previously hydrolyzed into small aggregates, a reaction which is improbable. At best, the final resin formed from phenol and hexamethylenetetramine cannot be formed by the mechanism which Dr. Baekeland suggests for the formation of Bakelite C which consists in the addition of  $\text{CH}_2\text{O}$  to a shorter chain to form an inner anhydride.

$\text{CH}_2\text{O}$  is not and cannot be present in a reaction between anhydrous phenol and hexamethylenetetramine. If water be formed, which, later, decomposes the hexamethylenetetramine to form  $\text{CH}_2\text{O}$ , 2.7 per cent would be required to produce enough  $\text{CH}_2\text{O}$  for the above reaction to take place, and we have shown that the total by-products formed in this reaction are at least 99.5-99.7-100.0 per cent pure ammonia, leaving on an average about  $1/10$  of the water necessary for the reaction, *i. e.*, if our gross error in determining ammonia be considered as entirely due to the formation of water (a supposition which has little probability behind it).

A further reason for holding to the chain formula is from the fact that the final resins whether formed from phenol and formaldehyde or hexamethylenetetramine are slowly soluble in normal caustic potash. This fact points to the presence of a free hydroxyl in the molecule of the final resin. The hydroxyl may be removed or filled with groups which make the resin inert toward alkalis.

For the sake of completeness, the following tables of constants for these resins have been added:

## PHYSICAL AND DIELECTRIC PROPERTIES OF THE RESINS

In the study of these resins for possible commercial uses the following constants have been determined:

*Tensile Strength*

The tensile strength of the pure resin is between 2000 and 4500 pounds per square inch depending upon the conditions under which it is made, such as temperature, pressure and time of heating.

The influence of temperature and time of heating upon the tensile strength are given in the following table:

TABLE I—TENSILE STRENGTH

No.	Time heated Hours	Temperature ° C.	Tensile strength Lbs. per sq. in.	Aggregate average showing effect in time Lbs. per sq. in.
4	1	123	1600	
8	1	146	1420	1646
12	1	181	1920	
5	1	129	1900	
9	1	155	1540	2050
11	1	179	2710	
6	1 1/2	128	2000	
10	1 1/2	150	2750	3050
14	1 1/2	181	4400	
7	2	127	1630	
11	2	150	3600	2716
15	2	183	2920	

By adding the values corresponding to a given temperature, the effect of temperature upon the tensile strength can be determined.

<sup>1</sup> Kraut, Beilstein, Seelheim, *loc. cit.*<sup>2</sup> Schroeder, Prinzhorn and Kraut, *loc. cit.*





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## A METHOD FOR DETERMINING THE AMOUNT OF ZINC CHLORIDE IN TREATED WOOD

By ERNEST BATEMAN

Received November 6, 1913

The need of a reliable method for determining the amount of zinc chloride in treated wood has already been mentioned in *THIS JOURNAL*. It was clearly shown in a series of wood-impregnation experiments recently conducted by the Forest Service. In these experiments maple and red oak ties were treated in three ways: (1) With zinc chloride solution alone; (2) with zinc chloride solution and creosote in emulsion; (3) with zinc chloride and creosote injected separately. The analytical method used until that time had given

excellent results for the soft woods, chiefly hemlock and tamarack, but when applied to the hard woods, particularly oak, it did not give concordant results, and failed entirely in the analysis of hard woods treated with zinc chloride and creosote in emulsion.

The method of analysis described in this paper is one developed to overcome the difficulties encountered. So far as known, the complete method has not been described before, although, in its separate parts, it is formed from a selection of certain well-known methods modified for this particular work. The problem that confronted the Forest Service in its experimental treatments necessarily confronts also many commercial treating plants and users of treated timber.

## SEPARATING INORGANIC SALTS FROM ORGANIC MATTER

A choice is offered of three possible methods of freeing inorganic salt in wood from the organic matter so that the usual inorganic methods of analysis may be carried out. These methods are:

I. Destruction of organic material by burning; estimating inorganic materials from the ash.

II. Removal of inorganic material by leaching or extraction with water, or dilute chemicals; analysis of the leaching solution.

III. Destruction of organic material by chemical means; analysis of the resulting solution.

## I. DESTRUCTION OF ORGANIC MATERIAL BY BURNING

This is the most simple method because it requires no special apparatus, but it is limited to those inorganic materials which are nonvolatile even at comparatively high temperatures. A portion of the inorganic salt would be lost, of course, if the temperature reached the volatilization point of the material. In spite of this limitation, the method is the one most generally used, and it is suitable for many inorganic materials. It should be remembered that certain metals, which in themselves are nonvolatile in an ordinary Bunsen burner, are volatile when in the form of chlorides. Iron and aluminum are notable examples. These metals and all of their salts, except halogen salts, are nonvolatile. The salts of zinc behave in the same manner, and the metal itself is volatile at about 1000° C. It is obvious, therefore, that a method of destroying the organic materials by burning can not be used in the estimation of zinc chloride.

In spite of these facts the idea is somewhat prevalent that this method can be used, and the following test was therefore made: Known amounts of a standard zinc chloride solution were added to 5 grams of dry sawdust, the excess of moisture carefully evaporated in a drying oven, and the wood ashed at as low a temperature as possible. Table I gives the results of these tests.

It is seen that at least 10 per cent less zinc chloride was found in the ash than was added to the sawdust, and in one case the difference was as great as 55 per cent. Further, there is no uniformity in the results, so that a factor for compensating for this loss can not be obtained. Any method, therefore, which includes the ashing of the wood is not reliable for zinc chloride determinations.



TABLE I—LOSS OF ZINC CHLORIDE IN THE DESTRUCTION OF WOOD BY BOILING.

Test No.	1 cu. ft. of dry wood saturated to weigh 50 lbs.		Zinc chloride added to 5 grams sawdust		Zinc chloride found in ash		Loss	
	Gram	Lbs. per cu. ft.	Gram	Lbs. per cu. ft.	Gram	Lbs. per cu. ft.	Per cent	
1.....	0.0417	0.2502	0.0383	0.112	0.0063	0.03	14.9	
2.....	0.0417	0.2502	0.0186	0.112	0.0231	0.138	55.3	
3.....	0.0834	0.5004	0.0616	0.369	0.0218	0.131	26.3	
4.....	0.0834	0.5004	0.0736	0.442	0.0098	0.058	11.7	
5.....	0.0834	0.5004	0.0673	0.404	0.0161	0.096	19.3	

## II. EXTRACTION OF ZINC CHLORIDE BY LEACHING

This method consists of extracting the zinc chloride by leaching with water (or dilute chemicals). For the following reasons no experiments were conducted in this method: (1) For complete extraction a considerable amount of expensive apparatus, such as Soxhlet extractors, would be required. (2) There is a possibility that all of the zinc could not be obtained even with prolonged extraction. (3) There would always be some soluble organic matter, such as tannins, sugars, etc., extracted with the zinc, which would have to be either removed or destroyed by chemical means. This operation could be performed on the original material as well as on the leached extract.

## III. DESTRUCTION OF ORGANIC MATERIAL BY CHEMICAL MEANS

METHOD PREVIOUSLY USED BY THE FOREST SERVICE—This method separated the zinc chloride from the wood through destruction of organic materials by chemicals. It consisted of the following steps: 5-10 grams of finely ground treated wood were digested in a Kjeldahl flask with 10 cc. of equal parts by volume of concentrated sulfuric and nitric acids. At the start, only a small flame was used under the flask, but as the foaming of the material subsided, the flame was gradually increased until the digestive mixture could be kept boiling constantly. From time to time, as the material became charred, more nitric acid was added until the solution remained water-white or pale yellow on boiling to sulfuric acid. With soft woods this point was reached in from 2-3 hrs., but with such woods as maple and oak the time was usually doubled, and frequently 8-10 hrs. were required for digestion. When creosote was present the solution sometimes failed to clear to a light yellow even after two days of digestion. Furthermore, in the subsequent analysis, it was frequently impossible to throw out with ammonium hydroxide the traces of iron which were always present; thus high results were obtained. The reason for the failure to digest creosoted material is not apparent, but it seems possible that, at times, conditions in the digestion flask were such that quinones and nitro bodies of anthracene and its homologues were formed which were not completely destroyed by sulfuric and nitric acids. An explanation of the failure of ammonium hydroxide to throw down iron in the dilute solution is equally hard to find, but it is supposed that sometime during the digestion one or more organic acids were formed. Iron compounds of these acids form double salts with ammonia which are soluble in

ammonium hydroxide. Whatever the reason, the fact is, that at times organic matter was present, and small quantities of iron remained in solution; hence the method was unreliable for the estimation of zinc. A further objection to the method is the extremely large amount of breakage of digestion flasks due to the severe treatment with boiling sulfuric acid. Furthermore, all the flasks tried by this method were attacked by the reagents, and either zinc, manganese, or some other interfering metal was dissolved, making it necessary to use a comparatively high correction to compensate for the flask. All kinds of glass are liable to this correction, but it is more nearly constant and smaller in amount when shorter methods of digestion are used.

IMPROVED METHOD—The details of the digestion method finally adopted are as follows: 5 grams of finely ground wood or sawdust are weighed into a 500 cc. short-neck, round-bottom Jena boiling flask; 50 cc. of a previously prepared saturated solution of potassium chlorate in concentrated nitric acid are then added in the cold and mixed with the sawdust by a vigorous shake. A violent reaction, accompanied by the evolution of considerable heat, immediately takes place, but subsides after a few minutes, leaving a wine-colored solution in which particles of partly digested wood are floating. When the solution has cooled somewhat, 10 cc. of concentrated sulfuric acid (sp. gr. 1.8) are carefully added and the solution again shaken. When this second reaction is complete the wood substance is all dissolved and the solution is of a dark red color. The solution is then boiled. At first the color becomes much lighter, but finally darkens to a brown. At this point more of the potassium chlorate-nitric acid solution is added and the solution kept boiling until no further charring occurs on evaporation to sulfuric acid. This boiling usually takes 1-1.5 hrs. after the digestion in the cold is started. In the course of 200-300 determinations, this treatment has not failed to give a clear solution free from organic matter and from which iron can be precipitated, if desired.

## ESTIMATION OF ZINC IN THE DIGESTION SOLUTION

CHOICE OF METHODS—The material having been digested to a form suitable for analysis, it was necessary to find some simple method of analysis with a fairly high degree of accuracy. The determination of zinc gravimetrically gives results more nearly correct than any volumetric method, but this method was not undertaken because, even in the hands of a trained chemist, it requires a large amount of delicate manipulation and is somewhat tedious and time-consuming. It was believed, moreover, that the extra time required for extreme accuracy would not be justified. Of the volumetric methods, those using potassium ferrocyanide as the titrating reagent are generally considered the best. Two methods using this reagent were tried, and were found to be about equally accurate. They differed from each other in the indicator used to determine the end point of the titration and in the preparation of the digestion solution for analysis.

**METHOD USING URANIUM ACETATE AS INDICATOR**—This method was the one commonly used. It is described in Sutton's "Volumetric Analysis" as "Fahlburg's" method, and consists of a titration with potassium ferrocyanide in hydrochloric acid solution, using uranium acetate as an outside indicator. This titration, to give the best results, must be carried out under reducing conditions; all nitrates, nitrites, and chlorates must be destroyed and iron must be removed.

The details of the method used in connection with the new digestion method are as follows: When the digested material remains clear after boiling for a few minutes to sulfuric acid, approximately 0.5 gram of solid sodium sulfite is dropped into the solution and the boiling continued for 5 minutes. This destroys all nitrates, nitrites, and chlorates, and also reduces any iron to ferrous compounds. The solution is then cooled and diluted with 100 cc. of cold water. The iron must now be reoxidized to the ferric condition by the addition of 25 cc. of bromine water and the solution boiled until all the excess of bromine is expelled. After cooling, and before filtering, the solution is made alkaline with ammonium hydroxide and set on the steam bath for about 1 hour to allow any iron present to settle. The filtered solution and the washing from the iron precipitate are neutralized with hydrochloric acid, and 5 cc. of concentrated acid in excess is added. The total volume is then made up to 175 cc. and the solution heated to 80° C. before titration. As a safeguard to make certain that the titration is carried out in a reducing solution, 25 cc. of saturated hydrogen sulfide water are added immediately before titration. Blanks on the complete method should be run, using dry, untreated sawdust or filter paper, and the correction for end point and the digestion flask should be subtracted from the readings in the analysis proper. It is usually not necessary to run more than duplicate or four blanks for even a large number of determinations, if the same standard solution is used; but blanks should always be run when the new standard solution is made up, unless it is exactly the same as the solution previously used.

**METHOD USING ACETIC ACID AND FERRIC CITRATE AS INDICATOR**—This method of analysis is a slight modification of the one used in the Sheffield Scientific School, Yale University. Potassium ferrocyanide is used as a standard solution, but the titration is carried out while the solution to be titrated is ammoniacal. Neither iron nor nitrates show any interference, but are added to the solution as an indicator; the necessity of removing them from the digested solution is, therefore, obviated and the titration can be carried out in the digestion flask. The end point of the titration is rather complex in theory, but very simple in practice. It depends upon the fact that ferric iron, in the presence of citric acid, is not precipitated by ammonia, but that a soluble salt, ammonium ferric citrate, is formed. The iron from this compound is not precipitated by potassium ferrocyanide in ammoniacal solution but is immediately thrown down when the solution is acid.

The details of the method are as follows: An outside indicator is first prepared of equal parts by

volume of glycerine and glacial acetic acid. The digestion mixture is then diluted with 100 cc. of water. Ten cc. of a 2 per cent ferric chloride solution and 10 cc. of dilute nitric acid and one gram of solid citric acid are then added and the solution allowed to cool; it is neutralized with ammonia and left slightly alkaline, and is then ready for titration. On account of the heat of neutralization of the acid with ammonia it is rarely necessary to heat the solution. It should, however, be about 80° C. at the beginning of the titration and its volume should be 200 cc. The end of the titration is reached when a drop of the solution placed in the center of a small portion of the glycerine acetic acid mixture appears as a blue or greenish blue circle. Blanks should be run as in the previous method.

**COMPARISON OF THE TWO METHODS OF TITRATION**—The accuracy of these two methods of titration is about the same, but the time required by the first method is twice as great as by the second. The second method can be used when phosphates are present with iron, a condition which frequently occurs in railroad ties which have been in service. For such a condition the first method would be unreliable, because the iron could not be removed by precipitation with ammonia, and part of it, at least, would be estimated as zinc. The second method has the further advantage of requiring no filtration, thus eliminating the chance for loss involved in this operation, especially in the hands of an untrained man. The results shown in Table II are as accurate as is required for routine testing of this nature, the error being not greater than 0.005 pound per cubic foot.

**ACCURACY OF THE COMPLETE METHOD**—In the tests in Table II, known amounts of zinc chloride were added to 5 grams of dry sawdust. The material was

TABLE II TESTS TO ASCERTAIN ACCURACY OF NEW METHOD FOR ZINC CHLORIDE IN TREATED WOOD

Test No.	Zinc chloride added to 5 grams sawdust		Zinc chloride found		Average		Average error		
	Gram	Lbs. per cu. ft.	Gram	Lbs. per cu. ft.	Gram	Lbs. per cu. ft.	Gram	Lbs. per cu. ft.	Per cent
1.....	0.0417	0.2502	0.0418	0.251	0.0412	0.247	0.0005	0.003	1.3
2.....	0.0417	0.2502	0.0406	0.244					
3.....	0.06255	0.3753	0.0619	0.370	0.06235	0.373	0.0002	0.002	0.7
4.....	0.06255	0.3753	0.0628	0.377					
5.....	0.0834	0.5004	0.0820	0.492	0.0827	0.496	0.0007	0.004	0.9
6.....	0.0834	0.5004	0.0834	0.500					
7.....	0.1043	0.6258	0.1034	0.6204	0.1038	0.623	0.0005	0.003	0.5
8.....	0.1043	0.6258	0.1043	0.6258					
Average error									0.85

analyzed by the last method described above and the results calculated as in Table I. The results obtained were in all cases a trifle too low. The maximum error, shown in these analyses, is 1.3 per cent and the average less than 0.9 per cent. This error certainly is no greater than that likely to occur in any method of preparing the sample for analysis from a piece of treated wood.

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## ON THE COMPOSITION OF GIANT KELPS

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The data presented in this paper were obtained in the course of the investigations directed by Dr. Frank K. Cameron, of the Bureau of Soils, looking to the possibility of the utilization of the giant kelps of the Pacific coast as an economic source of potash salts and other useful products.

During the summer of the present year, two parties were sent to Alaska for the purpose of surveying, mapping, sampling, and obtaining further information concerning the kelp beds of the Alaskan coast. One of these parties, under the leadership of Prof. G. B. Rigg, of the University of Washington, covered the beds of the Alaskan Peninsula; the other, headed by Dr. T. C. Frye, of Seattle, confined its operations to the coast of Southeast Alaska. The samples obtained by

TABLE I. (RIGG) RESULTS IN PROSECUTION

1, 2, 3, 8, *Alaria fistulosa*, 4, 5, X, 9, 10, *Nereocystis*, V, *Porphyra*, II, *Fucus*.

No.	Total sol	soluble salts	K <sub>2</sub> O	Ash	I	N	Locality
1a.....	15.44	2.27	4.41	None	2.44		
1b.....	15.76	2.61	4.44	None	2.35		Anchor Pt.
1c.....	15.16	3.08	4.72	None	2.44		Cook Inlet
1d.....	15.20	3.66	4.69	None	2.15		
2.....	25.72	5.99	6.04	None	2.10		Mogkag Isl.
3a.....	25.06	10.28	6.06	None	2.0		Putnam Bay
3b.....	20.14	7.05	7.08	None	2.84		Geese Isl.
8.....	30.62	12.70	6.46	None	2.88		N. of Hog Isl. near Alaska
4 Stem.....	52.88	28.26	3.60	0.06	1.06		Geese Isl.
5 Leaves.....	39.40	15.44	4.34	0.14	1.17		Geese Isl.
6a.....	18.80	20.21	1.12	None	1.8		Kodiak
9 Stem.....	36.40	21.69	3.10	0.06	1.10		Port Graham
10 Leaves.....	38.14	14.38	1.30	None	2.02		Port Graham
11.....	17.24	9.48	4.48	None	1.02		Seldovia
V.....	23.54	7.33	4.22	None	3.1		Geese Isl. Str.

(a) Whole young plant

both parties were dried, and sent thus in bags to the laboratories of the Bureau of Soils for analysis. The samples were run according to the methods published by Turrentine,<sup>1</sup> and results are given in Tables I and II. The nitrogen determinations in Tables I, II and III were made by T. C. Trescott, of the Bureau of Chemistry.

An inspection of these results indicates that the *Nereocystis* of Alaskan waters is, as respects potash content, of as great importance as an economic source of potash salts as that of the more southern waters. The *Macrocystis* contains a lower percentage of potassium than does *Nereocystis* while the *Alaria* contains a decidedly lower percentage. The sea-weeds *Fucus* and *Porphyra* are evidently valueless as sources of potash on an economical scale, and the analyses are given merely because of the interest which may attach to them otherwise.

Since the publication of the author's joint article with J. R. Lindemuth upon the leaching effects of sea water on freshly cut kelp,<sup>2</sup> a further set of analyses (Table III) has been obtained confirming the conclusions of that paper. A large sample of *Macrocystis*

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<sup>2</sup> This JOURNAL, 4, 141 (1912).

<sup>3</sup> Ibid., 5, 729 (1913).

TABLE II. (FRYE) RESULTS IN PROSECUTION

Genus and Species: 4, 8, 11, 12, 13, 15, 19 *Alaria fistulosa*;—20, 22, 23—1, 2, 3, *Macrocystis*, 6, 7, *Fucus*, 9, 10, *Nereocystis*, 14, 16, 17, 18, 21, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 100, 101, 102, 103, 104, 105, 106, 107, 108, 109, 110, 111, 112, 113, 114, 115, 116, 117, 118, 119, 120, 121, 122, 123, 124, 125, 126, 127, 128, 129, 130, 131, 132, 133, 134, 135, 136, 137, 138, 139, 140, 141, 142, 143, 144, 145, 146, 147, 148, 149, 150, 151, 152, 153, 154, 155, 156, 157, 158, 159, 160, 161, 162, 163, 164, 165, 166, 167, 168, 169, 170, 171, 172, 173, 174, 175, 176, 177, 178, 179, 180, 181, 182, 183, 184, 185, 186, 187, 188, 189, 190, 191, 192, 193, 194, 195, 196, 197, 198, 199, 200, 201, 202, 203, 204, 205, 206, 207, 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1836, 1837



After the large sample was cut at 2.10 P.M., it was taken from the water and kept out till 3.50 P.M. before re-immersion. It was cut off Pt. Vincente, California in the vicinity of the beds now being cut by commercial organizations, Lat.  $33^{\circ} 22' 30''$ , Long.  $118^{\circ} 20'$ .

Sub-samples 1-6 and 22 were taken where the large sample was cut; 7, while steaming to Pt. Vincente; 8-11, while steaming to Avalon; 12, on the way to San Diego; and the others in San Diego Bay

During the course of analysis of the numerous samples of kelps which have been recently analyzed in this laboratory, it was observed that in every instance, where stems and leaves of the same plant were separately analyzed, the total salt content, and similarly the potash content, in the stipe exceeded that of the laminae. This observation is of particular importance since Dr. Cameron in a recent<sup>1</sup> review of the kelp work, and on the basis of the analytical data then available for all stipes and all leaves, irrespective of the relations in individual plants, offered the opinion that there were no characteristic differences in this respect. Table IV gives a list of such samples

TABLE IV—RESULTS IN PERCENTAGES  
S = Stems; L = Leaves

Sample No.	K <sub>2</sub> O	Total soluble salts	Ash	N		
1 Macrocyctis	18.28	36.78	2.36	0.51	S	Coronado Isl., Lower Cal.
2 Nereocystis	9.90	25.94	3.88	0.84	L	Geese Isl., Alaska
	28.26	52.88	3.60	1.06	S	
	15.44	39.40	4.34	2.27	L	
3 Nereocystis	24.69	56.40	3.10	1.15	S	Port Graham, Alaska
	14.78	38.44	4.30	2.02	L	
4 Nereocystis	23.88	49.44	10.66	1.53	S	Pearse Canal, Alaska
	12.74	34.38	5.12	2.87	L	
5 Nereocystis	30.12	63.74	2.76	1.07	S	Bet. Tangass and Kanagunnt Isl., Alaska
	15.12	40.10	4.34	3.06	L	
6 Nereocystis	27.02	58.86	3.22	0.81	S	Gulf of Esquibel, Alaska
	19.63	47.26	3.46	1.04	L	
7 Nereocystis	28.76	64.44	2.90	0.59	S	Eagle Isl., David son Islet, Alaska
	16.74	42.74	5.66	1.52	L	
8 Nereocystis	24.80	53.54	3.68	0.98	S	Wrangell St., Alaska
	17.67	44.40	4.98	2.01	L	
9 Postelsia	20.0	41.1	4.0	1.01	S	Neah Bay, Wash.
Palmaeformis	13.9	29.90	5.7	1.83	L	
10 Postelsia	22.8	44.5	3.2	0.94	S	Montara Pt., Cal.
Palmaeformis	9.7	29.7	4.3	1.40	L	
11 Macrocyctis	18.7	40.3	5.3	1.24	S	St. Nicholas, Cal.
Pyrrifera	12.4	28.3	6.9	1.04	S & L	

Samples 9, 10 and 11 are from Turrentine.

with their respective analyses. An attempt to find uniformly constant variations between stem and leaves in content of other constituents justified the two following conclusions:

(I) The ash content is almost invariably larger in the leaves than in the stem of the same plant.

(II) The nitrogen content is almost invariably larger in the laminae than in the stipe of the same plant.

BUREAU OF SOILS  
U S DEPT OF AGRIC., WASHINGTON

#### THE ANALYSIS OF COMPLETE FERTILIZERS CONTAINING CYANAMID<sup>2</sup>

By H. W. HILL AND W. S. LANDIS

With the advent of new materials into the fertilizer

<sup>1</sup> Jour. Frank Inst., 176, 364 (1913).

<sup>2</sup> Presented at the 48th Meeting of the A. C. S., Rochester, September 8-12, 1913.

industry, there naturally arise new problems concerned with the analysis of mixtures containing the same. Such a new material is Cyanamid, now in its fourth season in the United States, though in much older use in Europe. That it is making remarkable headway in this country, is evidenced by the fact that last year's production will be doubled this year and some 60,000 tons will be placed upon the market next year.

At present, this material is marketed in two forms, a finely powdered Cyanamid, so finely divided that all will pass a 60-mesh screen, and 75 per cent or more will pass a 100-mesh screen; and a granulated form sizing between 10- and 80-mesh. The chemical composition of the two varieties is approximately the same, carrying nitrogen equivalent to 18.5 per cent ammonia, nearly all in the form of calcium cyanamide. This compound is a comparatively weak one, hydrolyzing instantly in an excess of water to cyanamide and its polymers, to ammonia, to urea, etc. The calcium salt is so unstable in the presence of water that it has never been isolated from aqueous solution.

Besides calcium cyanamide, the commercial product contains free calcium hydrate, graphite, and various other minor impurities. The product marketed last year averaged 40 per cent calcium content in the various forms enumerated above, which we are going to assume as hydrate for the purposes of this discussion since that is the form most probably assumed by the lime as soon as mixed in the ordinary complete fertilizer, though later it may react to various other forms.

Aboard, the bulk of the annual production of some 200,000 tons finds its way into the soil directly, due to the common European practice of using unmixed fertilizers. Only small quantities get into complete mixtures and no question of analysis seems to have arisen regarding such mixtures, as it is an assumed fact that there Cyanamid is incapable of transforming acid phosphates into an unavailable form, irrespective of the results yielded by the usual methods of analysis.

In this country where nearly all the Cyanamid enters into such complete mixtures which are sold on the basis of analysis by Official Methods, we have presented to us a possibility of reactions being caused to take place between the acid phosphate and the Cyanamid by reasons of the manipulation as prescribed in these methods of analysis. Results obtained after such reaction has taken place are of course not representative of the material as sampled.

We can here dismiss a discussion of the constitution of the ordinary acid phosphate of commerce. We have already discussed sufficiently the chemical constitution and behavior of Cyanamid, but it might be well to state here that our future discussion will be limited to the granulated form because of the present lack of a method of separating uncomposed Cyanamid from a complete fertilizer mixture other than by picking it out particle by particle. This granulated form of Cyanamid is designed to present a minimum of reacting surface for a maximum weight of material, the bulk of any addition to the ordinary fertilizer mixture remaining inactive in the interior of the granule.



A sample drawn for analysis, according to the Official Method from such a fertilizer mixture, is required to be ground, such grinding breaking up the granules. This broken-down mass is then treated with water in excess, liberating the lime of the former granule to action on the phosphoric acid, such procedure violating every principle upon which the inactivity of the granulated form of the Cyanamid was founded. The results of any such analytical procedure are not representative of the real conditions existing in the mixture as sampled.

Let us examine more closely the nature of the possible reactions taking place when acid phosphate and Cyanamid are mixed. The Cyanamid contains an equivalent of 74 per cent calcium hydrate which undoubtedly reacts immediately with any free acid in the acid phosphate to form a mono-calcium phosphate, such reaction being accompanied by the considerable heat evolution always noted on such mixing. The consequent high temperature of the mass, coupled with the water content of the same, may even cause the hydrate to react with the mono-calcium phosphate to form the di-calcium phosphate, but as far as we can ascertain by other than chemical analysis, we do not believe this second reaction progresses very far, or that it takes place at all in cold, dry mixtures. In proof of this last contention we have mixed sufficient Cyanamid with acid phosphate to neutralize the free acid and left the pile to cool. After cooling more Cyanamid was added to the mass without sign of a second reaction caused by this second addition. The same result was obtained with a complete fertilizer mixture, the first addition of Cyanamid serving to neutralize the free acid and dry out the mass, and no further reaction took place on second addition, as evidenced by thermochemical and physical observation. Analyses by the official method, however, have shown an apparent loss of availability on this second addition, thus furnishing another reason for questioning its applicability to a Cyanamid mixture.

Believing as we do that reaction will take place between free calcium hydrate and acid phosphate during the chemical manipulation of analysis by the official methods, particularly where the calcium hydrate has been locked up in granules of Cyanamid, we determined to try a few experiments to substantiate these views. The grinding and the leaching with water put both the lime and the phosphoric acid into solution and reaction will ensue causing precipitation in both the filter and the receiving beaker, according to conditions. Any precipitation of phosphoric acid in the filter means a low result for water-soluble. Digestion of the water-insoluble residue with neutral citrate in the presence of the hydrate again causes reaction and precipitation as insoluble during the digestion, giving results for insoluble phosphoric acid having no relation to the content in the original sample. We are even of the opinion that the neutral citrate digestion breaks up calcium carbonate if present and causes precipitation of insoluble phosphoric acid, though it will not react with the mono-calcium phosphate either dry or in water solution.

In order to substantiate our theory regarding the hydrate we performed the several experiments. An acid phosphate analyzing by the official method 0.29 per cent insoluble  $P_2O_5$ , condition fairly dry, was used in all the experiments.

I. Into the point of four dry folded filters were placed, respectively, 0, 0.25, 0.75 and 1.00 gram of dry calcium hydrate. On top of each were poured quickly 2 grams of the above acid phosphate and analysis according to the Official Methods started immediately. No chance for mixing or reaction was given. The results obtained were as follows:

Weight of Hydrate	Insoluble $P_2O_5$
Gram	Per cent
0	0.29
0.25	0.28
0.75	4.54
1.00	4.47

The lime remained in the point of the filter in one lump and probably represents the extreme case of one large granule of unreacted Cyanamid in acid phosphate. Our experience with acid phosphate mixtures would lead us to believe that absolutely no reaction had taken place between the hydrate and the acid phosphate before the first water was added.

The other extreme of the powdered Cyanamid acid phosphate mixture conditions would be approximated by mixing the hydrate and the acid phosphate in the filter. This was done in the next experiments.

II. A very quick rough mix was given the acid phosphate hydrate mixture before adding the water. No indication of reaction having taken place here was apparent.

Weight of Hydrate	Insoluble $P_2O_5$
Gram	Per cent
0.11	0.29
0.11	13.40

From the results of these two experiments we conclude that if free Cyanamid or free calcium hydrate in any form are present at sampling, the Official Methods of Analyses do not yield results indicative of the actual conditions in the pile at the time of sampling. The apparent loss of phosphoric acid in an actual mixture, as determined by this official method, would lie somewhere between the results as indicated in Experiments I and II, because the conditions existing in the original pile as to distribution of the hydrate is somewhere between the extremes of the one large granule and the more even distribution of the hydrate, but there is no doubt that it does become quite serious.

It is a very simple matter to prove the existence of free hydrate in a fertilizer mixture containing granulated Cyanamid by actually picking out the granules of unreacted or undecomposed Cyanamid. Other means of attempting to ascertain the degree to which the Cyanamid reacted on the acid phosphate in a complete fertilizer mixture failed. Two mixtures studied from a thermo-chemical standpoint showed approximately that three-quarters of the powdered Cyanamid and one-third of the granulated Cyanamid had entered into reaction, but we look upon this as

essential thermo-chemical data. We have not, at this time, found a mechanical or chemical method of isolating the undecomposed Cyanamid particles from a complete fertilizer mixture, other than by hand-picking, which at best affords a partial separation of the coarser particles.

As a concrete example of the proof of such undecomposed Cyanamid present in a fertilizer mixture might be cited the case of a ten-ton batch made up as indicated below:

FORMULA	PER CENT $P_2O_5$ IN	
	ACID PHOSPHATE	GARBAGE TANKAGE
1000 acid phosphate	Free acid..... 3.64	
125 granulated Cyanamid	Water-soluble..... 12.64	0.15
200 muriate of potash	Citrate-soluble..... 4.53	2.55
300 garbage tankage	Available..... 17.17	2.70
375 filler	Insoluble..... 0.29	1.19
	Total..... 17.46	3.89

This batch was stored in a bin, surrounded on all sides by similar bins containing similar mixtures, and the center of the mass rose  $70^{\circ}C$ . in four days after mixing, and then slowly cooled off. Six weeks after mixing, a sample was drawn while still warm to the hand, from which sample we picked out sufficient undecomposed Cyanamid for analysis. This Cyanamid was clean and free from adhering acid phosphate, which really seemed to have as great an affinity for the garbage tankage as for the Cyanamid. The separation in this manner offered difficulty only because of the presence of the dark-colored particles of the tankage and the dark colored filler used, and not because of adherence of the acid phosphate. An analysis made directly on the particles, as separated without attempting to clean them off in any way, gave 48.5 per cent calcium hydrate and 0.15 per cent phosphoric acid, showing the presence of the hydrate in the particles as sampled. The granules of Cyanamid showed decomposition of the cyanamide and the presence of moisture, which probably is the cause of the lessened percentage of hydrate found in them.

We have endeavored to show here that the Official Methods of Analysis give results in no way indicative of the character of the sample as taken where free calcium hydrate or Cyanamid is present in the mixture. Such results show an apparent loss of availability that has no real significance as far as concerns the condition of the material before analysis. Granulated Cyanamid remains for a large part unacted upon even in additions as high as 300 Cyanamid to 1000 acid phosphate and at temperatures as high as  $110^{\circ}C$ . It is more decomposed in the manipulation incident to analysis by the official methods than in the mixing with the acid phosphate, if we can believe the results of some recent investigations we have made.

We regret that we cannot offer a solution to this problem, which not only concerns the Cyanamid industry, but the larger fertilizer industry as a whole who have been striving to use limestone fillers in their mixtures for the great beneficial effects following the use of such fillers. The use of such material is now prohibited because of the great loss of availability shown on analysis by the Official Methods. We believe that it is impossible for calcium carbonate, as well as the hydrate we have worked with, to transform

an acid phosphate past the dicalcium stage under the ordinary conditions of mixing and batching of the semi-dry materials employed to-day. But we do know that the digestion with neutral citrate will cause reaction of any free hydrate with the di-calcium phosphate at that stage of the manipulation, and the same must be true of the carbonate, though we have not made a direct investigation to prove this statement.

In our own work we have found that the dilute weak acids frequently recommended for analysis of the Basic Slags show practically no loss of available in acid-phosphate mixtures containing up to 300 pounds of granulated Cyanamid and 1000 pounds of acid phosphate to the ton of complete mixture, even though the temperature of the mass rose to over  $110^{\circ}C$ . and remained high for many weeks. Such methods do show a loss of available for additions of powdered Cyanamid much in excess of 125-150 pounds to the 1000 of acid phosphate, though this amount has, in many cases, been exceeded by a proper choice of inactive diluents in the complete mixture. The results of analysis of Cyanamid acid phosphate mixtures by these last-named methods agree more closely with other physical and thermo-chemical data than do those obtained by the Official Methods.

We believe the great importance of a comprehensive study of the reactions between acid phosphate and calcium hydrate and calcium carbonate under the mixing conditions existing in actual fertilizer practice would lead towards a solution of the use of a limestone filler for fertilizer mixtures, and everyone appreciates the great agricultural advantage to be derived from the use of such a material in the industry. The problem should be approached from several angles, not all purely chemical, as we have shown the failure of a chemical method to produce results characteristic of the material worked upon in our case as described above.

NAGARA FALLS, ONTARIO

#### A STUDY OF THE MILK OF PORTO RICAN COWS

By HOWARD J. LUCAS, R. DEL VALLE SÁRRAGA AND J. ROMÁN BENITEZ  
Received September 15, 1913

This work was undertaken for the purpose of determining how, and to what extent, the milk from the native Porto Rican cows varies from that of other countries, and to what extent the use of different grasses as food affects its composition.

The so-called native cow does not seem to be of any particular breed, but appears to be the result of the mixing of different strains introduced into the island from time to time. There seems to be no attempt on the part of the people to divide the cattle into different breeds on the basis of color, and consequently no attempt has been made to do so in this work.

The value of cattle in Porto Rico does not depend entirely upon its use as a source for meat and for milk, but rather upon the fact that the oxen form the most common beast of burden, and are used in all parts of the country for performing the heaviest kinds of work, such as hauling, plowing, rough farm labor, etc.

It is only natural to suppose, then, that the utility of the cow as a milk producer has been lost sight of to a greater or less extent, and emphasis has been placed upon the desirability of raising oxen for agricultural purposes. Therefore, it is reasonable to conclude that but little attention has been given to the improvement of the stock for milk production by suitable methods of breeding.

The peculiar manner of milking is undoubtedly an unfavorable factor in milk production. This is done but once in every twenty-four hours, and then under conditions which must always be complied with. The cows have been so bred and so accustomed to this method of procedure that they refuse to let down milk otherwise. The calf is first allowed to start the flow of milk and is then removed, the milk-man continuing the operation until he has obtained all that he possibly can. The calf is again allowed to suckle, and it is often possible to obtain a second milking by again removing it, although it is not customary to do so in the large dairies. All this involves a great waste of milk, and a loss of labor and time necessary for handling and herding the calves during the milking process. Such an unscientific method has a decided influence upon the fat content, which might vary considerably, depending upon whether much or little of the strippings are secured.

As but little grain is fed, the cows are kept in the pastures the year round. Certain sections of the island, notably the southern half, receive rain for a part of the year only, and during the remainder suffer from drought. During these periods the pastures dry up, and the cattle suffer from lack of food. This condition naturally leads to decreased production of milk, and this factor, together with the peculiar custom of milking, and the deterioration of the strain through lack of proper breeding, has brought the native cow of Porto Rico to a state of low efficiency as a milk producer. Daily yields run from 1-10 or 12 qts. and 5 is considered a good average.

This condition can not be attributed to the prevalence of disease; on the contrary, it is a well known fact that the cattle of the island are remarkably free from tuberculosis, and have strong resisting powers against those diseases to which they are liable.

With the exception of work done by R. del Valle Sárrega (office of Health, Charities and Correction, Chem. Laboratory, Bul. No. 2) on samples of milk from two cows at stated intervals, there have been no published analyses of milks of known purity from cows on the island. It was hoped that this work might prove to be a guide for establishing a standard for Porto Rico.

**COLLECTION OF SAMPLES:** At first it was the intention of the authors to collect the samples personally, but later as it became desirable to obtain them from all parts of the island, the Director of the Laboratory issued a circular requesting the health officer of each municipality to forward two samples of milk of known purity to the laboratory. They were directed to personally supervise the milking of two cows, taking care to have the milking complete, and the whole

thoroughly mixed before withdrawing the sample, consisting of 250 cc. To the latter was to be added five drops of a 40 per cent formalin solution before sending to the laboratory.

The following data in regard to each sample were requested:

Quantity of milk (specimen preserved)  
Date of milk  
Time of day  
Kind of feed given to cow

It was further requested that, if possible, one cow should be six months or more calved, and the other two months or less. Due to a misunderstanding, many officials sent wrong data for the quality of milk. It follows from the above that the value of this work depends upon the reliability of the men who collected the samples, and it is felt that they have accomplished their work in a conscientious manner. The samples were collected from December to May, the majority during February.

**ANALYSIS OF SAMPLES:** The samples were taken with a Quevenne lactometer, which had been standardized against the Westphal balance. Proper corrections were made for the temperature when other than 15.6° C.

The fat was determined according to the method of Babcock.

Total solids were determined by evaporating five grams of milk to dryness in a platinum dish on the water bath, and heating for four hours at 100° C. in the water oven. Previous experiment had shown that constant weight was obtained at the end of this time, but the results may be low, as the residue was often more or less brown. On a number of samples total solids were not determined by drying, because at one time the milks came in so rapidly that facilities for so doing were lacking. The dry residue was burned off in the muffle furnace at a low red heat and weighed as ash. Solids were calculated on all samples by the use of the Richmond slide rule. Lactose was determined polariscopically, using acid nitrate of mercury as the clarifying agent.<sup>1</sup>

The refraction of the copper serum was taken according to the method of Lythgoe.<sup>2</sup>

#### INTERPRETATION OF RESULTS

Table I gives the results of analyses, tabulated according to fat content, of some typical milks, selected from a list of 140 analyses, which lack of space prevents giving in its entirety. Solids-not-fat are calculated from solids by drying when given, otherwise from solids by calculation. Table II gives the maximum, minimum and average of each determination. Under total solids are included solids by drying, and of such the solids by calculation were used for calculating solids-not-fat. The percentage of fat is seen to vary within exceedingly wide limits, from 0.8 per cent to 10.2 per cent; total solids also have a wide range. The maximum for solid-not-fat, ash, lactose, and refraction of copper serum are exceptionally high, showing that certain of the milks could be heavily watered without being detected by chemical means.

U. S. DEPARTMENT OF AGRICULTURE, BUREAU OF CHEMISTRY, 1913



TABLE I TYPICAL MILKS (FAT-LACTOSE IN PERCENTAGES)

Date	Age of cow Yrs.	Time since calving Mo.	Kind of food	Volume of milk Qts.	Specific gravity (15.6° C.)	Fat	Total solids by calculation	Total solids by drying	Water	Solids-not-fat	Ash	Lactose	Refraction copper serum 20° C.
4-18-13	4	6	C. G.	1	1.0330	10.2	20.66	20.66	79.34	10.46	0.80	5.01	39.4
3-29-13	4	9	Gr. M.	1	1.0337	8.6	18.9	19.04	80.96	10.44	0.85	4.00	38.5
2-18-13	5	2	G.	3	1.0285	8.0	16.9	17.00	83.00	9.00	0.66	4.82	38.1
2-6-13	6	6	M.	7	1.0313	6.8	16.1	16.17	83.83	9.37	0.74	4.79	37.9
2-10-13	7	6	P.	7	1.0318	6.6	16.0		84.0	9.4		4.57	38.3
4-16-13	5	2	P.	7	1.0340	6.3	16.2	16.58	83.42	10.28	0.73	4.94	39.6
2-7-13	8	6	P.	2	1.0305	5.8	14.75		85.25	8.95		4.85	37.8
4-23-13	4	6	M. G.	1	1.0323	5.4	14.7	15.36	84.64	9.96	0.75	4.52	36.8
2-11-13	5	1	G.	4	1.0370	5.0	15.4		84.6	10.4		5.09	39.2
1-20-13	10	6	M.	10	1.0348	4.4	14.15	14.04	85.96	9.64	0.77	5.30	39.0
5-21-13	5	7	P.		1.0380	4.1	14.55	14.85	85.15	10.75	0.84	5.07	38.8
5-15-13	3.5	1.5	M.		1.0302	4.0	12.5	12.64	87.36	8.64	0.63	4.77	36.9
4-30-13	3	5.5	M.	4	1.0350	3.9	13.6	13.43	86.57	9.53	0.75	4.92	38.5
5-14-13	4	6	Ma.	3	1.0342	3.7	13.15	13.24	86.76	9.54	0.63	5.43	38.5
2-17-13	7	6.5	G.	7	1.0330	3.4	12.5	12.34	87.66	8.94	0.76	4.61	37.4
1-20-13	9	1	M.	7	1.0370	3.0	13.0	12.68	87.32	9.68	0.76	5.67	40.0
5-23-13	5	6	M.	5	1.0347	3.0	12.4	12.27	87.73	9.27	0.71	4.75	37.9
5-23-13	4	1.5	Gr.	7	1.0315	2.9	11.8	11.17	88.83	8.27		4.75	37.6
4-21-13	3	2	P.		1.0342	2.6	11.8	11.78	88.22	9.18	0.73	5.02	37.4
2-24-13	4	2	P.		1.0330	2.1	11.0	10.82	89.18	8.72	0.68	4.81	37.3
4-30-13	5	1.5	M.	7	1.0376	1.6	11.55	11.36	88.64	9.76	0.77	5.26	38.9
4-18-13	8	7	G.		1.0353	1.0	10.2	9.98	90.02	8.98	0.79	4.29	36.5
4-21-13	7	8	P.		1.0346	0.8	9.75	9.40	90.60	8.60	0.78	4.37	36.9

(a) G. = yerba de guinea (guinea grass). M. = malojillo. P. = pasto común. Gr. = grama. Ma. = matojo.

Table III gives the analyses of those milks which showed abnormally low results in one or more deter-

TABLE II

	Sp. gr. 16.6° C.	Fat	Total solids	Water	Solids-not-fat	Ash	Lactose	Refraction copper serum
Maximum.....	1.0386	10.2	20.66	90.60	10.75	0.86	5.67	40.0
Minimum.....	1.0285	0.8	9.40	79.34	8.27	0.63	4.00	36.0
Average.....	1.0337	4.22	13.63	86.37	9.42	0.74	4.99	38.28

minations other than fat and total solids. Although Nos. 1, 2, and 3 have all the appearance of being wa-

also grama and matojo; pasto común may be a mixture of any of these, and is used to designate any ordinary pasture containing different varieties of grasses. The average for cows fed upon guinea grass is much higher than for those fed upon the others. Those milks from cows fed upon more than one kind of pasture are not included in this table.

SUMMARY—This work is the first of a series of analyses to be made for the purpose of determining a standard for Porto Rican milk.

TABLE III—ABNORMAL MILKS

Date	Age Yrs.	Time since calving Mo.	Kind of food	Volume of milk Qts.	Specific gravity (15.6° C.)	Fat	Total solids by calculation	Total solids by drying	Water	Solids-not-fat	Ash	Lactose	Refraction copper serum (20° C.)
4-23-13	4	4.5	P.	1	1.0249	4.2	11.4	11.45	88.55	7.25	0.55	3.64	33.4
5-20-13	4	4.5	P.	1	1.028	2.6	10.3	10.22	89.78	7.62	0.59	4.14	34.2
5-20-13	6	11.0	P.	2	1.023	5.3	12.25	12.71	87.29	7.41	0.51	3.51	32.6
5-13-13	4.5	3.5	P.	1	1.0301	3.1	11.4	11.28	88.72	8.18	0.63	4.22	35.2
5-11-13	12	6	G.	2	1.0288	3.2	11.15	10.82	89.18	7.62	0.69	4.11	37.6

tered, investigation has shown that they are genuine milks, and duplicate samples, taken by special inspector, gave similar results. If the standard for milk in Porto Rico were made to include milks which give results as low as those in Table III, it would allow watered milk to be sold extensively. Further work

TABLE IV—EFFECT OF FOOD UPON FAT CONTENT

Kind of food	Per cent			No. of samples
	Maximum	Minimum	Average	
Guinea grass.....	10.2	1.0	4.71	22
Malojillo.....	7.8	1.3	3.98	44
Matojo.....	3.7	3.7	3.7	1
Pasto común.....	7.0	0.8	3.37	53
Grama.....	3.8	2.9	3.35	2

is necessary in order to determine the prevalence of those milks with abnormally low constants.

Table IV shows the effect of feed upon fat content. Guinea grass (yerba de guinea), malojillo, and pasto común are the pastures most in use. Guinea grass and malojillo are separate and distinct grasses, as are

The native Porto Rican cow is milked but once daily, and gives a small yield of milk. Factors which conduce to this are: (1) Deterioration of strain through inattention to proper breeding; (2) improper milking methods; (3) insufficient food during certain seasons.

The cattle are remarkably free from tuberculosis. The milk may vary within wide limits as regards total solids and fat content, and may run exceptionally high as regards solids-not-fat, ash, lactose, and refraction of copper serum. Certain milks ran exceptionally low in one or more determinations, and these were discarded from the standard until further work could be done. Guinea grass seems to be the best adapted as a pasture for cows, the fat content averaging considerably higher in the milks from cows so fed. Further work should be done, particularly with milks taken during the summer months.

CHEMICAL AND BROMATOLOGICAL LABORATORY  
SAN JUAN, PORTO RICO



A STUDY OF AMERICAN GROWN BELLADONNA<sup>1</sup>

By F. A. MILLER AND F. N. RICE

A study of the experiments upon belladonna culture in the United States indicates that the quality of the drug produced based upon the percentage of total alkaloids has been fair but extremely variable. Most of these experiments have been conducted upon a small scale, though some attempts have been made at commercial production.

Rippetoe<sup>2</sup> reports upon a few plants grown in the Shenandoah Valley, Virginia, where belladonna was found to be fairly hardy. His assays indicate that the leaves from first-year plants grown in this locality contained 0.23 per cent of alkaloids, the second year leaves 0.68 per cent, one average plant (leaves) 0.48 per cent and the roots from the same plant 0.38 per cent. Schneider<sup>3</sup> reports upon drug grown at San Francisco, California, which assayed 0.40-0.80 per cent for the leaves and 0.50 per cent for the stem. He also grew some plants at Salina, California, which he claims gave a high yield. Unfortunately, we are left in doubt as to the exact nature of this "high yield" and cannot say whether he referred to relative amount of drug produced or to the alkaloidal yield. Again<sup>4</sup> in 1911 there is a meager report upon drug grown near Oakland, California, which is said to have been of "very high quality." Also in the 1912 report<sup>5</sup> from the same region the author states that he is satisfied the crop of that year will show a high percentage of alkaloids, perhaps 0.75 per cent or more. Further, he states that some of the belladonna leaves and stems from this locality have yielded as high as 0.84 per cent. It is to be regretted that more accurate data have not been given on these experiments. Sayer<sup>6</sup> gives the following assays on California-grown belladonna: leaves 0.64 per cent, stems 0.29 per cent, small stems 0.43 per cent and coarse stems 0.16 per cent, average 0.51 per cent. He quotes manufacturers as having found a variation of from 0.35 per cent to 0.84 per cent of alkaloids in drug from this state, with an average of 0.64 per cent. Englehardt<sup>7</sup> gives a series of very high figures on California drug: leaves 0.83 per cent, stems 0.85 per cent and a mixture of leaves and stems 0.79 per cent. Evans Sons, Lescher & Webb<sup>8</sup> find 0.40 per cent in leaves and 0.16 per cent in stems from drug of commercial source. Borneman<sup>9</sup> describes briefly his experiments in Pennsylvania and gives assays of 0.58 per cent for leaves, and 0.53 per cent for roots from first-year plants.

In contrast with the foregoing experiments, which have been quite general as to purposes and results, is the work of Chevalier<sup>10</sup> on the effects of various fertilizers upon the percentage of alkaloids in belladonna and other solonaceous forms, of Ransom and

Henderson<sup>1</sup> who have studied the influence of meteorological conditions in addition to that of commercial fertilizer and of Carr<sup>2</sup> who in addition to the last-named factors has performed experiments which include the light relation and its bearing upon the production of alkaloids in belladonna. In this manner the influence of environment upon the physiology of the belladonna plant is being investigated. A review of the assays recorded by various workers upon commercial belladonna for the past fifty or sixty years indicates that the alkaloidal value of this drug may range from 0.00 per cent,<sup>24</sup> to 1.32 per cent<sup>4</sup> in the leaf and from 0.10 per cent<sup>6</sup> to 0.86 per cent<sup>7</sup> in the root. These latter figures indicate still greater possibilities in the production of alkaloids in cultivated belladonna than have yet been attained.

However, it is evident from a thorough review of the experiments upon this plant as well as medicinal plants in general, that not all means of developing them to their maximum have as yet been exhausted. It seems that the most neglected of these is the opportunity for the production of improved varieties by breeding and selection. Most of the valuable economic plants have been obtained through selection, hybridization, and adaption. Few such forms have ever been produced through an application of the methods now being used to grow medicinal plants. It has been found that economic forms once brought to a high state of development must be intensively and continuously bred in order to retain them in this condition. Medicinal plants will doubtless be found to behave in a similar manner.

The behavior of active principles in selected plants and the influence upon them of various methods of breeding, together with a study of the essential factors of growth, are some of the possibilities which have led to the following experiment.

One-third of an acre was planted to belladonna in the following manner: Seeds were taken from a shipment of commercial belladonna leaves (No. 24712) and sown in the greenhouse, February 2, 1912, in seed pans. These germinated March 1st, and soon afterwards the seedlings were transplanted to flats and retained in the greenhouse until April 15th when they were transferred to cold frames. The young plants hardened off in these frames until May 20th. They were then four inches or more high and were transplanted to the open field. The soil was a stiff clay loam which had been cropped severely for a number of years. Cultivation was necessarily frequent on account of the poor physical condition of the soil. By July 12th the plants were flowering freely. As strong vigorous plants came into flower the best appearing individuals were selected and numbered. These were inbred, i. e., close pollinated in order to obtain seeds of known origin. Samples of leaves from these selected, inbred plants were collected for

<sup>1</sup> Paper presented at the 13th meeting of the A. C. S. Milwaukee, March, 1913.

<sup>2</sup> Rippetoe, *Am. J. Pharm.* **79**, 835 (1907).

<sup>3</sup> Schneider, *Proc. Am. Pharm. A.* **57**, 833 (1907).

<sup>4</sup> Schneider, *Pract. Pharm.* **5**, 187 (1911).

<sup>5</sup> Schneider, *Ibid.* **6**, 189 (1912).

<sup>6</sup> Sayer, *Ibid.* **4**, 332 (1909).

<sup>7</sup> Englehardt, *Proc. Am. Pharm. A.* **58**, 136 (1910).

<sup>8</sup> Evans Sons, Lescher & Webb, *Ind. Eng. Chem.* **1906**, 7, 8.

<sup>9</sup> Borneman, *Am. J. Pharm.* **84**, 881 (1912).

<sup>10</sup> Chevalier, *Compt. rend.* **100**, 914 (1910).

Roots	37	1907
Leaves	27	1907
Stems	1907	1907
Leaves	74	1906
Stems	74	1906



The usual calculations for direct stress on the seams of this digester (Fig. 2) do not indicate a stress likely to produce rupture.

Thus, where

$P$  = internal pressure, taken as 100 lbs. per sq. inch, to cover the gauge pressure, the hydrostatic pressure of the contents, and any slight fluctuation above the normal.

$r$  = inside radius of the digester shell = 84 inches.

$t$  = thickness of the steel shell = 1 inch.

$f$  = circumferential stress in the shell, in lbs. per sq. inch.

$$f = \frac{Pr}{t}$$

$$\frac{100 \times 84}{1} = 8400 \text{ lbs. per sq. inch.}$$

and the longitudinal stress =  $\frac{Pr}{2t} = 4200$  lbs. per sq. inch.

Taking a single pitch length of  $4\frac{7}{8}$  inches on the vertical seam, the sectional area of the plates is reduced by rivet holes as follows:

$$\text{Shell plate, } \frac{3.314}{4.875} = 0.6792 \text{ of full pitch section.}$$

$$\text{Cover plate, } \frac{3.3625}{4.875} = 0.7308 \text{ of full pitch section.}$$

Hence the direct stress in tension in the vertical seam becomes for the shell plate,  $\frac{8400}{0.6792} = 12,370$  lbs. per sq. inch, and for the cover plate ( $1\frac{1}{8}$  inches thick),  $\frac{8400}{1.125 \times 0.7308} = 10,220$  lbs. per sq. inch.

For the girth seam, by a similar process, the stress in tension is for the shell plate, 6750 lbs. per sq. inch, and for the cover plate, 5480 lbs. per sq. inch; hence the circumferential tension on the shell plate is the greatest, and assuming an ultimate tensile strength of plate 55,000 lbs. per sq. inch, the factor of safety in tension is  $\frac{55,000}{12,370} = 4.45$ .

Within the  $4\frac{7}{8}$  inch pitch length, there are three rivet sections in single shear. Assuming a shearing strength of 45,000 lbs. per sq. inch in the rivets, the shearing resistance on one pitch becomes

$$3 \times 3.1416 \times 1.3125 \times 1.3125 \times 45,000 \div 4 = 182,600 \text{ lbs.}$$

The load on one pitch is  $8400 \times 4.875 = 40,950$  lbs., therefore, the factor of safety in shearing the rivets becomes  $\frac{182,600}{40,950} = 4.46$ , so the lower factor of safety is apparently that in tearing the plate between rivets, or 4.45.

Attention is now naturally directed toward the material of which the digester was constructed. For the purpose of forming an estimate of the suitability of this material, specimens were taken for chemical and physical tests, with the following results:

Carbon Per cent	Sulfur Per cent	Phosphorus Per cent	Per cent
0.18	0.016	0.013	0.37
0.22	0.016	0.015	0.37
	0.016	0.013	0.41
	0.016	0.015	0.40
0.21	0.020	0.015	0.41
0.22	0.017	0.021	0.37
0.23	0.018	0.012	0.35
0.20	0.016	0.021	0.37
0.21	0.016	0.013	0.38

Phosphorus	0.037
Manganese	0.420
Sulfur	0.020

Comparison with the specifications of the American Society for Testing Materials shows that the shell sheet falls within their recommendations, while the cover plate fulfils the specifications except in the matter of carbon, which is somewhat in excess—tending to give a harder and less ductile steel than is ordinarily used in boiler work.

Physical tests were made at the McGill University Laboratory, with the following results:

Physical properties	Specimen 1	Specimen 2	Specimen 3
Ultimate strength, lbs. per sq. inch	55,700	55,600	56,300
Elastic limit, lbs. per sq. inch	10,700	16,700	16,900
Yield point, lbs. per sq. inch	26,900	27,000	27,000
Elongation in 8 inches	28.8%	29.4%	32.6%
Reduction in area	57.9%	57.9%	58.7%
Modulus of elasticity	32,800,000	30,000,000	26,000,000

For comparison with the foregoing, the following tests were also made upon  $1\frac{1}{8}$  inch steel recently furnished for similar purposes:

Physical properties	Specimen 1	Specimen 2
Ultimate strength, lbs. per sq. inch	64,000	64,000
Elastic limit, lbs. per sq. inch	15,000	13,700
Yield point, lbs. per sq. inch	31,000	31,000
Elongation in 8 inches	31.1%	31.1%
Reduction in area	50.6%	53.0%
Modulus of elasticity	29,000,000	29,000,000

(a) No pronounced yield point, but a gradually increasing yield after the elastic limit was passed.

In both of the foregoing tests, the American Society for Testing Materials specifications are satisfied except for the yield point, which is low. The elastic limit, or limit of proportionality of stress to strain, however, is very low in both the old and the new material, ranging from 10,700 to 16,900 lbs. per sq. inch in the former, and from 13,700 to 15,000 lbs. per sq. inch in the latter. This characteristic of low elastic limit will be brought up later in the calculation of total stresses.

Subsequent investigations of the other vertical cover plates and of those removed from digesters of similar design and service revealed cracks starting between the rivet holes along the inner vertical row—precisely where failure occurred in the ruptured seam. The nature of the cracking is indicated in Fig. 3, which represents a piece of cover plate broken apart by blows from a sledge hammer. The shaded portion



shows the location of cracks which had started near the rivet holes, largely on the inner side of the plate.

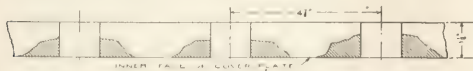


FIG. 3.

The general nature and location of these cracks pointed strongly to a failure by repeated bending of the cover plate under stress. While measurements on the inside of a similar digester showed a slight flattening of the curve near the seam, due probably to difficulty in the bending rolls, this peculiarity would prove rather a benefit than an injury, since the tendency of the cover plate is to take this formation under stress. The line of resistance in cylindrical shells under internal pressure tends to conform to the circle and since the single outside cover plate construction throws this line of resistance outside of the true circle, the tendency under stress is to restore it by bending the cover plate inward, as illustrated in Fig. 4.

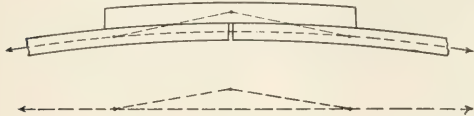
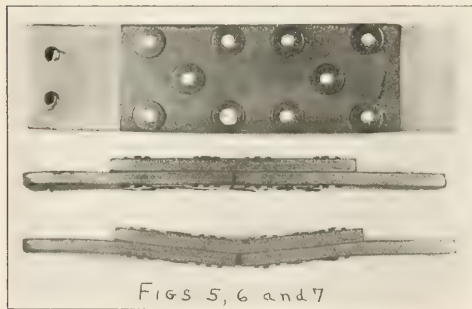


FIG. 4.

To exhibit this action more clearly, a one-fourth size rubber model of a section of this seam was made, as seen in Fig. 5. Fig. 6 shows a profile of the model before tension was applied, and Fig. 7 indicates clearly



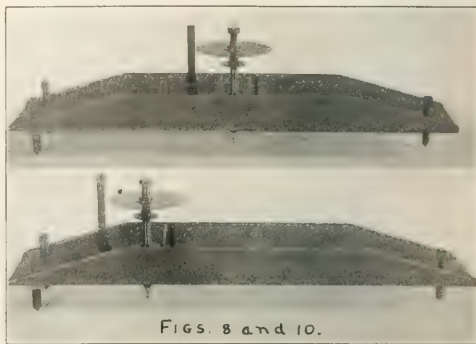
Figs. 5, 6 and 7

the effect of tension on the seam. Particular attention is invited to the concentration of bending between the inner rows of rivets, corresponding in the full size seam to a span of about 3 inches.

This evidence naturally led to a desire to determine, if possible, the nature and extent of the inward deflection of the vertical cover plate under working conditions, and for this purpose a deflection gauge was devised, as shown in Fig. 8.

The frame of the instrument was made from a piece of 4-inch steel channel bar. The set screws constituting the legs are of hardened tool steel. The two

at the left end are pointed, while the single one, at a distance of 17 inches from the first two, is slightly rounded. The pointed legs are forced into the cover plate near its outer edge, by light blows when the instrument is first in place, so that in subsequent readings it is necessary only to set the pointed legs back into

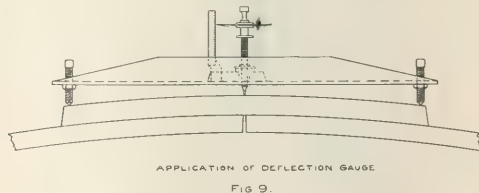


Figs. 8 and 10.

these little depressions to insure an exact reproduction of the original setting.

The cover plate is polished where the single rounded screw-leg rests, as are also the spots where the micrometer measurements are made.

Fig. 9 indicates the method of application of the instrument for measurements of deflections at the center of the 17-inch span. The micrometer is firmly fixed in the center of the instrument frame for this setting, and in making observations, the micrometer screw is advanced until the sense of touch lightly indicates that its point rests upon the polished plate.

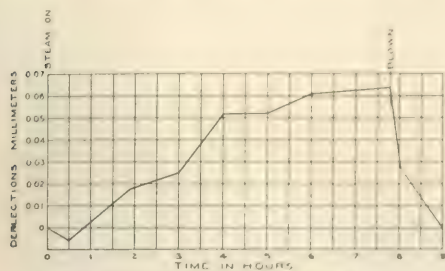
APPLICATION OF DEFLECTION GAUGE  
FIG. 9.

In exploring the curve formed by the deflections in the cover plate the micrometer was relocated at a point 4 inches off-center, as shown in Fig. 10.

Measurements were taken at intervals ranging from thirty minutes to an hour, starting before the steam was turned on and continuing for at least half an hour after the digester was blown. The diagram, Fig. 11, which is typical, presents a graphical record, on a time base, of the deflections observed at the center of the 17-inch span, while that of Fig. 12 is for a point 4 inches off-center.

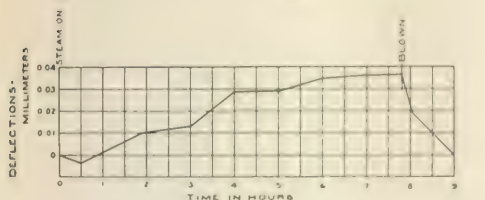
The maximum deflections obtained in the tests represented by Figs. 11 and 12 are replotted on the diagram in Fig. 13, on a base line representing the 17-inch span. The ordinates at the center and at points 4 inches off-center are plotted to a magnified scale and the smooth curve drawn through these points

shows the nature of the deflection. As forecast roughly in the behavior of the rubber model, the concentration of bending is almost exactly over a span of 3 inches in the middle portion. The deflection at the center of the 3-inch span is found to be 0.0003 inch.



INWARD DEFLECTION OF VERTICAL COVER PLATE -  
CENTER OF 3 INCH SPAN

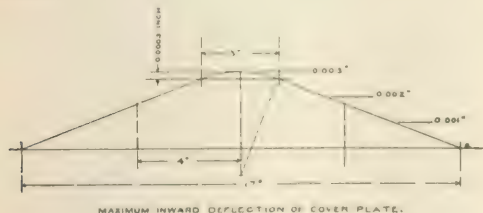
FIG. 11



INWARD DEFLECTION OF VERTICAL COVER PLATE -  
AT POINT 4 INCHES OFF CENTER

FIG. 12

Just why the cover plate should persist in bulging out slightly immediately after the steam was turned on the digester, following the recharge, as shown by the negative deflection in both diagrams, was at first a troublesome question, and called for further investigation.

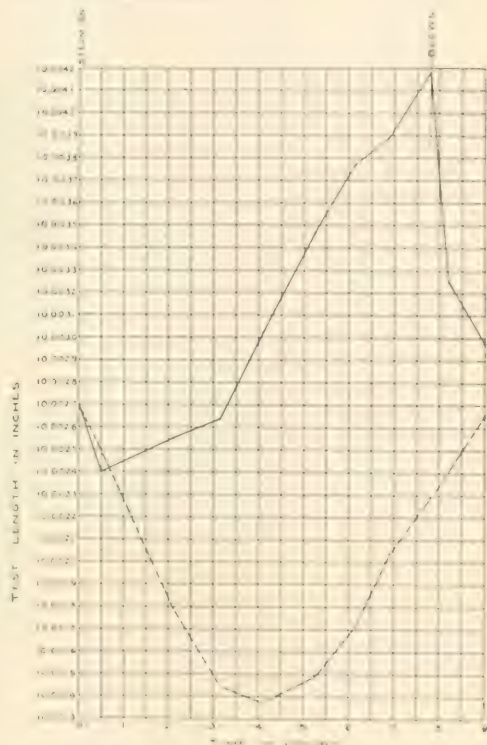


MAXIMUM INWARD DEFLECTION OF COVER PLATE.

FIG. 13.

Since these deflections were assumed to be the result of circumferential stress in the shell, it seemed reasonable to suppose that if some sort of extension gauge were applied to the shell sheet in this region, the corresponding stress could be readily calculated. For this purpose, a Howard strain gauge was applied at the same height on the digester as the deflection gauge, and midway between the vertical seams of the adjacent sheet. This strain gauge is in reality a special micrometer capable of indicating within 0.0001 inch error any change in length between two small carefully prepared holes drilled 10 inches apart. Where the modulus of elasticity of steel is 30,000,000, an extension

of 0.0001 inch represents a tensile stress of 300 lbs. per sq. inch. This test length was taken along the circumference, and readings were made simultaneously with those of the deflection gauge, together with the shell temperatures obtained from a thermometer sealed to the shell sheet. The results of these readings are shown in full lines on the diagram, Fig. 14, while the dotted lines indicate how this test length would have varied under the influence of temperature alone. It was, of course, prevented from so varying by the internal pressure, therefore the distance measured up from the dotted line to the full line gives the extensions due to internal pressure.



— STEAM GAUGE READINGS THROUGHOUT COOKING  
— CHANGES IN OTHER TEST LENGTH ON ACCOUNT OF TEMPERATURE  
— SHOWN (DOTTED)

FIG. 14

To exhibit more clearly what is going on during a single cook in the digester, a combination diagram, Fig. 15, has been plotted with diagrams A, B, C, and D on the same time base.

Diagram A gives a graphical record of the temperatures inside the digester, the shell temperatures, and the temperatures at a point in the middle of the brick lining. The latter were obtained by drilling a small hole through the shell and half way through the lining. Into this hole a thermometer was inserted and carefully packed with fiber to isolate the bulb from outside conditions. An important feature of

this diagram is the fall in temperature of the middle of the lining and of the shell after the steam was turned on, continuing for two or three hours, and finally rising again. This is due to the chill of the recharge and the slow transference of heat in the brick and cement lining.

Diagram B is plotted from the pressure chart, and the figures at the left show the pressures in pounds per square inch during the cook, while the figures at the right show the corresponding calculated stress in the shell, and the maximum stress—between rivet holes—in the cover plate, respectively.

On diagram C the full line indicates the stretch in the 10-inch test length calculated from the pressure

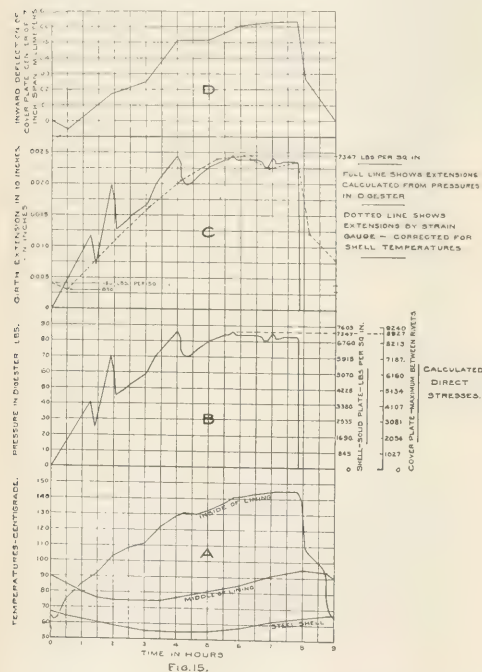


FIG. 15.

in diagram B, while the dotted line shows the stretch in this test length obtained from the strain gauge readings, corrected for shell temperatures as explained in connection with Fig. 14. The maxima of the two curves are placed as nearly coincident as possible in order to show how nearly back to zero the dotted line will come; in other words, how nearly back to rest the shell plate will come, at the beginning of the cook. It will be noted that there appears to be 1180 lbs. per sq. inch residual stress in the shell sheet at the time when the steam was turned on, falling to 850 lbs. per sq. inch half an hour later and then rising slowly to the maximum.

For convenience of comparison, diagram D, showing the corresponding deflections at the center of the cover plate, is plotted immediately above C. It is at

once noticed that the cover plate began its inward deflection exactly half an hour after the steam was turned on and simultaneously with the beginning of stretch in the shell, shown dotted in diagram C.

Thus far we had established the relation in action between the girth tension in the shell and the inward deflection of the cover plates, but the reason why the stress relaxed for a short time, or for any time at all, after the steam had been turned on the digester, had not been explained. It was felt that in some way the expansion of the brick lining had something to do with the case, and it had even been suggested that this expansion may have been able to produce an excessive stress upon the seam. That the latter assumption is incorrect is shown, first by the fact that the strain gauge did not indicate a greater stretch in the shell than would be expected from the internal pressure; and again, from the following separate investigations

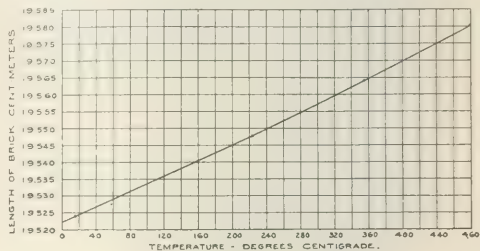


FIG. 16.

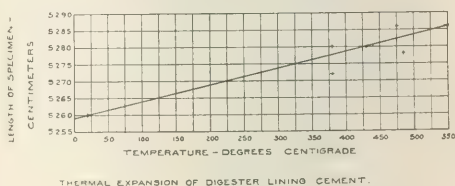


FIG. 17.

of the characteristics of the brick and cement of the lining:

A sample of the brick similar to that used in the lining of this digester was selected for determining its thermal expansion. This brick was polished at points on its ends, and slowly heated in a gas furnace in contact with the thermo-junction of a LeChatelier pyrometer, and its length measured every few hours with a delicate micrometer. The result of this experiment is shown graphically in Fig. 16. Similar tests were applied to a cube of lining cement, with results as shown in Fig. 17. From these, the coefficient of thermal expansion of the brick was found to be 0.0000068, and of the cement, 0.00000927 per degree Centigrade.

From diagram A of Fig. 15, the maximum temperatures attained by the inside and middle of the lining, and by the steel shell were replotted in Fig. 18 on a base to represent the thickness of the digester wall, and a smooth curve drawn to show the fall in tem-



perature from the inside to the outside of the digester.

The mean temperature of each layer of the lining, taken from Fig. 18, was now utilized to determine

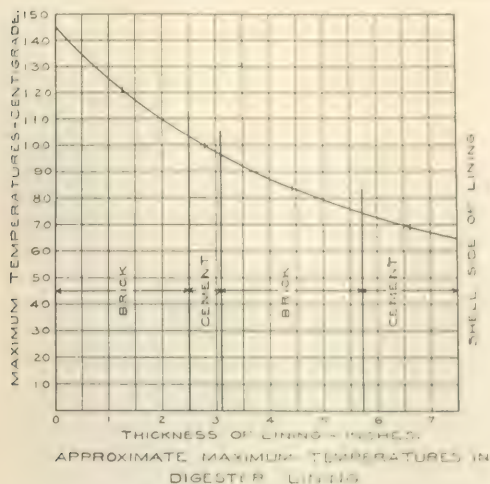
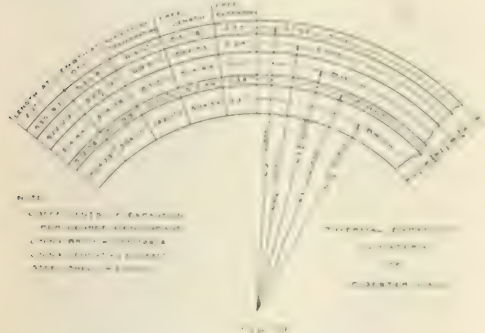


FIG. 18

the amount of expansion in each case for the entire circumference—assuming the layers free. The results of this calculation are given in the last column of Fig. 19 under the heading "Free Extension."

It will be noticed that the circumference of the shell will extend 0.25 inch during the cook, while the average extension of the inner two layers of the lining would



be 0.34 inch, if allowed to expand freely. At the most, this would give a difference of 0.09 inch to be accommodated between shell and lining in the entire circumference of the digester. It can be readily shown that this has no effect, since if the shell extends 0.0024 inch in 10 inches, due to internal pressure (see diagram D, Fig. 15), then in the circumference of the digester there would be a total extension due to pressure alone— $2\pi r \times 0.0024 = 0.0048 \times 10 = 0.048$  inch, which lifts the shell clear of any possible crowding by the lining while the pressure is on.

When the digester is blown, however, the removal

of internal pressure causes the shell to contract, and it therefore settles back upon the lining, which at this time is expanded to its maximum by heat. Diagram A, Fig. 15, shows the temperature of the middle of the lining to be decreasing after the steam has been turned on, with consequent contraction, so the shell now follows the lining back until internal pressure again lifts the plate away from the lining. This accounts for the curious action of the shell and cover plate for the brief period at the beginning of the cook.

Where the shell is shrinking back upon the lining, the latter would be expected to compress more than the former to stretch for a given force, and it was with a view of determining the exact relation that the moduli of elasticity of both brick and cement were obtained from compression tests at the McGill University Laboratory. Results of these tests are shown in the following table:

Properties of materials	Brick	Cement
Ultimate compressive strength	8,770	4,800
Modulus of elasticity	3,080,000	1,150,000
Length tested for compression	4 inches	1 1/4 inches

Thus the modulus of elasticity of the steel is about ten times that of the brick lining; in other words, a given section of brick would compress ten times as much as an equal section of the shell would stretch, within the elastic limit of the weaker material.

#### TOTAL STRESS

Proceeding now to the calculation of maximum stress in the cover plate, it will be recalled from the diagram, Fig. 13, that the maximum deflection at the center of a 3-inch span was found to be 0.0003 inch. Making use of the general formula for the deflection of beams of uniform section, within the limits of proportionality of stress to strain.

$$\Delta = \frac{W L^3}{48 E I}$$

$$E I = \frac{W L^3}{48 \Delta}$$

Where:

- $\Delta$  = deflection of beam at point of maximum deflection
- $L$  = length of beam
- $W$  = weight of beam
- $E$  = modulus of elasticity of material
- $I$  = moment of inertia of beam
- $M$  = bending moment at point of maximum deflection
- $S$  = section modulus of beam
- $y$  = distance from neutral axis to extreme fiber

$$A = \frac{M}{S} = \frac{W L^3}{48 \Delta S}$$

$$S = \frac{W L^3}{48 \Delta A}$$

$$S = \frac{W L^3}{48 \Delta A}$$

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$$S = \frac{W L^3}{48 \Delta A}$$

Adding to this the maximum direct stress in the cover plate,  $4,500 + 10,220 = 14,720$  lbs. per sq. inch, the

maximum repeated stress on the inner side of the cover plate.

Reverting to the results of tensile stress on material from the shell of this digester, and from new material used for similar purposes, it will be recalled that the true elastic limits were shown to range from 10,700

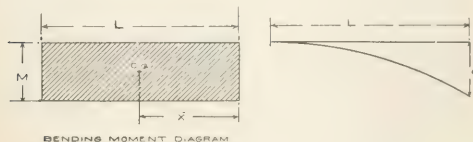


FIG. 20.

to 16,900 lbs. per sq. inch. Since the true elastic limit, rather than the ultimate strength, is a vital

consideration in repeated stresses such as we are dealing with here, the fact that the maximum fiber stress of 14,720 lbs. per sq. inch falls within the range of elastic limit of the material is most significant. No steel will endure for an unlimited period a repeated stress even slightly above its elastic limit. In this case it took fourteen years of repetition of the stress to cause rupture, but the same action is present in all digesters of similar design—the stress varying in magnitude with the thickness of the cover plate and the pressures carried. Where this stress is shown to exceed the elastic limit of the material of the cover plate to any extent whatever, ultimate failure from repeated bending must be expected.

McGILL UNIVERSITY  
MONTREAL, CANADA

## GERMAN OBSERVATIONS ON OUR INDUSTRIES

### WHAT DID WE CHEMISTS LEARN IN AMERICA?<sup>1</sup>

By B. RASSOW

"He who would understand the poet must go to the poet's country." ("Wer den Dichter will verstehen, muss in Dichters Lande gehen!") These words of Goethe are applicable not only to the appreciation of the poets of a foreign country, but also to the general comprehension of its inhabitants and more particularly of its industrial life.

It is said of us Germans, that we have in us a special nomadic impulse. Doubtless this impulse to travel is traceable not only to esthetic motives, but also to our craving to learn how other peoples think and work. That our own science and technique are greatly advanced thereby is a matter of course.

Of all industrial countries, there is no doubt that the United States of America are at present of the greatest interest to us Germans. The conditions under which technical work and manufacturing are carried on in North America are, in some respects, very similar to our own, but in others, very different from them.

It is hardly possible to imagine a greater difference, than we find between the activity of the German manufacturer, who can hardly move, in our old and densely populated country, without being hampered by police ordinances and by the rights of his neighbors—who is forced by the state to care for his employees on a large scale, even in times during which the employee is of no further use to him—and, on the other hand, the American manufacturer, unrestricted by all such considerations and fetters.

But the great similarity between American industry and our own is doubtless caused, in part, by the fact that our industry is in reality just as young as that of the United States. The modest beginnings of factories, which came into existence in some of the German states 200 years ago or more, are only insignificant germs of the mighty development of German industry, which has really been established for only about 100 years.

The beginnings of American industry also date back about 100 years, *i. e.*, to the time when the United States became politically and commercially independent, when manufactured goods were no longer procured exclusively from the English mother country, and home manufacture was begun instead. There, then, as with us, we see in the last century the conversion of an agrarian state into a political organism, in which, until a few years ago, agriculture and industry still possessed about equal importance for the entire political economy, while at present the conditions are continually becoming more favorable to industry.

<sup>1</sup> Address delivered at the Annual Meeting of the Verein Deutscher Chemiker, Breslau, Sept. 18, 1913. Translated by The Chemists' Club Library from *Zeitschrift fuer angewandte Chemie, Aufsatzteil*, 26, 1913, p. 705.

Many of us German chemists, when preparing for the journey to North America a year ago, hardly realized these reasons for the special interest which every German must feel towards the United States and her industry. Doubtless, however, the great longing which drives progressive German scientists and technologists to the United States, is traceable to this line of reasoning. But I should like to refer at the very beginning to one essential difference. Germany is a country having a civilization many centuries old, which, up to the middle of the 19th century had, it is true, manifested itself essentially in literary and esthetic spheres. It is quite otherwise with America. There, the beginnings of civilization do not extend back much more than two centuries. During the last century the majority of the immigrants were poorly educated workmen—men who lacked all literary and scientific training and all advanced technical knowledge. Therefore we cannot be surprised that, in many sections of the Union, in spite of wealth, a finer appreciation of culture appears only in the second or third generation.

We chemists made the journey across the ocean principally on account of the Eighth International Congress of 1912. Though we are accustomed to seeing Germany well represented in the international chemical congresses, this was especially the case at the Eighth International Congress. A good half of the non-American participants in the Congress came from Germany. The reason for this is naturally to be found as much in the magnificent development of the German chemical science and industry, as in the German impulse for study and travel. To be sure, we know that several of the European countries, *e. g.*, England, are still ahead of us in many branches of the chemical industry, especially in inorganic manufacture. But in no country on earth are those branches of the chemical industry which demand versatility of thought, and particularly a large body of scientifically trained employees, so well developed as with us. Our synthetic dye, synthetic drug, and perfumery industries are foremost throughout the world, and there is probably no country in which the heads of factories are so imbued with the conviction that their employees must needs cast a glance beyond domestic boundaries. That our government authorities willingly aid its employees in the study of foreign institutions, is well known. Accordingly, we counted among the German participants in the Congress no small number of professors of chemistry and technology and appointees of various national government bureaus.

But those colleagues whom we met there were also largely of German extraction, or had studied in Germany. Thus it





men. The only advantage derived from this by factory superintendents is that strikes are usually not so extensive as in old Europe. For the most part, the various races of which the working force is composed, are at odds with one another, so that one-half continues to work merely to annoy the other. However, it is well known what power the organizations of skilled laborers—the trade unions—exercise in the United States, and how they force the manufacturers and public opinion—aye, even the legislative bodies—to take their demands into consideration.

I should like to consider somewhat more in detail the school and educational conditions in the United States, and the favorable opportunities for obtaining a higher education. Tuition in general elementary schools is free; this is the logical consequence of compulsory school attendance. If the young man goes from the elementary school into business, then, according to my observation, he has more and better chances to continue his education than in our country, notwithstanding all the advanced schools in our large cities. New York City possesses an especially exemplary arrangement for advanced instruction in the College of the City of New York. This college is not a university, but an advanced school, in which thousands of better qualified young men and women receive instruction every year, enabling them to obtain good and even advanced business positions. In the great Assembly Hall of this college, which is built like a mighty cathedral, the general lectures of the Eighth International Congress were held. It is characteristic that in all schools, but especially in such advanced schools, a specific American patriotism is instilled into the children. This discloses to us the secret of so many American successes and peculiar qualities. From the beginning of his schooling the child brought up in America, be his origin ever so little American, is taught to regard America as the land of freedom, and as the country in which all is arranged in the best manner. Even if later experiences cause much to appear different to the mature man, unlimited respect for all American institutions and productions remains the key-note of all his thinking. We have sometimes laughed over the fact that every important edifice was represented to us as the greatest in the world, or at least as the best and most expensive. But there is method in thus inculcating a special respect for the achievements of the country and its inhabitants. I wish our Germans, and especially our German workmen, had somewhat more of this way of thinking.

We cannot truthfully say that the workman in America is essentially better off than here. Certainly, in some of the large cities of the Union, more opportunities are given him to own his home, and to become more independent than in Europe. But so far as the factory owner is concerned, he is regarded, after all, only as so much horsepower, which is paid for so long as it works, and is then pitilessly cast aside. In America there are no welfare provisions of any kind for workmen, such as there are in Germany. Although the wages are much higher than with us, many of the necessities of life are so much more expensive that it is difficult for even an economical workman to provide for illness and old age. If the living and working conditions of New York City and Chicago are observed, the conclusion is reached that our factory workmen enjoy, on the average, better living conditions than the American workmen.

Let me return to the means of achieving a higher education, which, according to my observation, are especially well provided for in America. Hardly a week passes without our reading in the newspapers that one of the multimillionaires has donated one or several million dollars to a public library, a museum, a university, or a high school. This seems to me like a kind of auto-taxation on the part of these trust magnates. They know that the United States covers the principal part of its budget by means of import duties. The many high duties on manufactured goods and raw materials make it possible for the great industrial manufacturer to amass immense wealth, while at the

same time the most necessary requirements of the whole people become very much more expensive. Of the great fortunes which are accumulated by so small a number of individuals, then, a very considerable part is returned to the people in the form of donations for a great variety of cultural purposes. How many magnificent foundations we have seen! It is well known that the buyers for the American museums and libraries, at all auctions in Europe, constitute a direct danger to our stock of artistic and literary treasures. But how beautifully are these treasures displayed in America, and how easily accessible! All the museums I saw are open until 8 or even 10 P.M. All are provided with arrangements for artificial illumination and heating, so that progressive employees and workmen can devote several hours, after the close of the working day, to further education along the lines of art, science and literature. Accessibility in the late evening holds good not only for the public libraries, but also for the great scientific libraries and museums of all kinds. In this direction we can really learn much. Instruction is also imparted to ambitious people from eight until ten or eleven o'clock evenings, and not only by lectures, but also by practical exercises in natural science (especially chemical branches).<sup>1</sup> One representative of a great dye stuff factory told me the progress of his education from a young apprentice in a store, with only a common school education, to a chemical merchant of the foremost rank. His practical knowledge of chemistry he owes chiefly to evening courses. You have surely all read in the papers of American students who earn their livelihood and the wherewithal for studying by cleaning streets. Even though I did not become acquainted with such students, yet in Atlantic City, in one of the great bath-houses, we became acquainted with a doorkeeper of the individual bath-houses, a medical student, who, by this well-paid confidential position, earned enough money in four months to enable him to study during the rest of the year. I am sure that none of his American fellow students finds anything degrading in this. That "work is no disgrace" is still more true in America than among us.

I should like to depict to you a few more good aspects of a truly democratic commonwealth, which struck me in the United States, and above all the self-control which the American evinces on all public occasions. To the man who has once seen the migration of nations, which begins daily at the close of business hours from the city of New York to the widely scattered suburbs, in which hundreds of thousands of the employees live—to him all the magnificent traffic arrangements—subways, street-cars, and elevated railroads must seem totally inadequate, and it is a fact that at those hours every means of traffic is filled to twice and three times its capacity. But with what wonderful quietude the departure of these hundreds of thousands takes place! No crowding and no haste, because each one knows that he will not hasten progress thereby, but will, on the contrary, hamper it. How few policemen are necessary to direct and guide this movement! How little are the trammelen annoyed with questions which they could answer just as little as our own officials! On a trip in the neighborhood of Pittsburgh, we stopped a whole hour before a bridge, just before reaching the Pittsburgh Station. Not one of the Americans in the car with us asked a single question of the train crew. Each one knew that the track would be cleared as soon as possible, and that, until then, all questions and restless running about were absolutely useless. This self-control depends upon the fact that the public is supervised as little as possible in all traffic arrangements. If, instead of the 60 people provided for, 120 or 130 should be carried in one of the cars of a subway train, it does not concern any policeman. If people walk on the railroad tracks, it does not concern any employee. To be sure, prohibitions are posted, but, as a matter

<sup>1</sup> In several large German cities, especially in Hamburg, Berlin and Frankfurt on the Main, there are similar arrangements, but still not to the same extent as, for example, in New York or Boston.

of fact, this serves only to guard the directors from claims for damages. I do not wish to represent American railroad conditions as entirely ideal. I am firmly convinced that, in most respects, our arrangements are better. But, with respect to a certain ease and dexterity in dealing with the public, our courts and officials could learn much. We would in the long run progress further by these methods, than under the present system of guardianship.

While thus far I have spoken to you principally of what struck me as worthy of imitation, and as actually typical of the United States, I cannot pass over some of its unpleasant aspects. The haste with which the American is accustomed to pursue his work and pleasure is well known. However, I cannot say that the work, as a whole, is benefited by this haste, which is usually followed by a corresponding depression. Even if the American generally has very good nerves, and is able to bear great over-exertions as well as great distractions, through noise and unrest of all kinds, nature will nevertheless have her revenge sooner or later, for, in spite of all training, the American is only a human being. This great and unproductive haste is closely connected with that prodigality with natural treasures, which is universal in America. These resources, as you know stand at the disposal of the United States in almost unlimited abundance. You know that the American soil contains coal of all kinds, in such quantities that, in spite of the high cost of labor, a good hard coal does not cost much more than a dollar a ton at the mine and not more than \$10 to \$12.50 in New York, in spite of the high cost of transportation. The same is true of soft coal. You know that ores of nearly all important metals are found in great quantities in the central and western states.

I need not tell you of petroleum and natural gas, of phosphates and sulfur; all are found in abundance, and are energetically exploited. But this very abundance, and the high cost of labor, easily led the American technologist to squander the treasure. The mining of coal and ores is often carried on in such a way that a fourth and even a third of the minerals remain in the mines, because these portions are somewhat more difficult to remove, and because the handling as well as the preparation, would make the cost somewhat higher. This neglect of thorough exploitation has already given much concern to far-seeing Americans. Institutions have been created like the Bureau of Mines, which, by means of fine scientific and technical apparatus and large sums of money, are working towards the rational removal of treasures of the soil.

It is well known that the Americans are careless in the utilization not only of their mineral treasures, but also of their arable land. The virgin ground of the Eastern States, which the Pilgrim Fathers wrested from the wilderness and its inhabitants, and which was then planted with grain year in and year out, has long since been exhausted, because proper fertilization was neglected. The billows of wheat have already reached the Rocky Mts. In the Eastern States large tracts, which were exhausted and devastated by decades of corn cultivation, are now being replanted with forests. In this respect also, the Americans have much to learn from our old country. Rational fertilization, especially by artificial fertilizers, is spreading farther and farther in the United States. Phosphates exist in enormous quantities. Nitrogen fertilizers are still obtained in great measure from Chili, but the time will come when all American coke plants will utilize their by-products, furnishing ammonia salts for purposes of fertilization. Furthermore, the plants already installed for manufacturing atmospheric saltpeter and calcium nitride are being enlarged, and will then furnish the necessary material for nitrogenous fertilizers. Only potassium salts are lacking. We felt that it is truly painful to the Americans, that this important fertilizer has not yet been found in any sufficiently large quantity in the Union, and that for this material, at least, America must remain dependent upon Germany. An

entire meeting of the Inorganic Section of the International Congress was devoted to the potash question, without the appearance of any possibility of independence of German potassium

If, then, the American farmer is forced to fertilize artificially in the same measure as the European, all productive and commercial conditions will be changed not a little, and obviously not to our detriment.

You are probably surprised that, in this summary of mine, so little has been said of chemists and the chemical industry, but I have already stated in my introduction that, in accordance with American conditions of labor and production, only the inorganic manufacturing industry is really well developed, and that even there work is done, for the most part, by methods which are known and familiar to our German colleagues. Certainly our colleagues in the chemical process have much of great interest, as for example at the Parke Davis plant in Detroit, at the General Chemical Co., in the Acheson Works, etc., but I should prove ungrateful were I to report on them in detail, since these matters are, for the most part, considered as business secrets.

The greatest gain which we have obtained from the American trip, need not be sought in these special fields, but rather in the universal broadening of our knowledge and observation in every industrial and cultural line. But the gain in this respect was all the greater and finer, as the Americans met us with wonderful hospitality and cordiality. It may be true that a subtle touch of braggadocio was one of the reasons for our being shown so many fine plants and arrangements, secrecy about which would be demanded by stern business interest. In any case we owe our American friends lasting gratitude for what they permitted us to see, and for the friendship which we enjoyed. Thus, many a visit was made, in accordance with the rules of the Congress, on the basis of reciprocal courtesy. I think I can assure you in the name of the participants in the Congress and in the trips, that this reciprocity will not only be carried out by us according to the "rules," but that we shall always be pleased to receive visits from our American colleagues in order to return like for like. That German chemical science has, ever since Liebig's time, been a source of the greatest information to the Americans, was constantly and willingly acknowledged by our American colleagues.

And I must express my thanks still further. You know that our society, under the leadership of our former president and present honorary member, Geh. Reg.-Rat Prof. Dr. C. Dussberg, decided, two years ago, in Stettin, to found a Jubilee Fund, by means of the first installments of which a number of German chemists were sent to the Congress in America. We fourteen chemists, to whom an opportunity was thus given to broaden our point of view in an unexpected degree—who, as chemists as well as men as technologists, as well as professors, learned an infinite amount—owe lasting gratitude to the "Verein deutscher Chemiker," and to the founders and donors of the Jubilee Fund.

#### IMPRESSIONS OF THE EIGHTH INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY IN NEW YORK AND OF CERTAIN FIELDS OF INDUSTRY IN THE UNITED STATES

The following report of my five weeks' stay in the United States is a description of my impressions of the general details, and of the organization of the Congress held in New York in September.



1912. This I shall give before referring to the material collected in my inspection of certain special industries.<sup>1</sup>

### Impressions of the Congress

The preparations for the New York Congress, as for its predecessors, were made well in advance. Long before, chemists interested in the Congress were supplied with printed details of the measures taken toward the organization, not only in New York, but also on the part of the German Central Committee charged with the work of preparing for the Congress and which held its first meeting in Berlin as early as July, 1911, while its office was located in Leipzig. Announcements 1 to 4 supplied the members with a gradually increasing fund of information concerning the form of the Congress, the articles to be read, the sight-seeing tours to be made, and to these were appended excellent maps describing the technical visits and the various possible excursions. Very special care was also taken on the part of the New York Committee for the success of the Congress. All branches of the work of organization did not, however, meet with equally good results.

Especially to be mentioned is the painstaking organization of the technical tours which extended as far as California and the Mexican border. These matters were in the experienced hands of Dr. D. T. Day of Washington and Dr. Geo. D. Rosengarten of Philadelphia, and according to the testimony of all the participants in these trips they were a brilliant success.

Considering the expense of the trip from Germany to New York it was said that considerable reductions would be afforded for the round trip as an inducement for the coöperation of the German members. The rebates, however, shrank from time to time to scarcely perceptible amounts and then only for the outbound trip and this was only procured after considerable vexation combined with much correspondence on the part of both the New York and the Leipzig Committees. Thus, finally, it came to be regarded by many as a distinct advantage to be an ordinary passenger on the "Cleveland" and not a member of the Congress claiming any special concession for a place on this or any of the boats. It need not be mentioned that various unpleasant things were said about the steamship company concerning this feature of the organization.

In spite of these troubles at the outset of the trip, we arrived safely in New York on the "Cleveland," the "George Washington" or other ships after an interesting and pleasant voyage. On the "Cleveland" a storm delayed us a day. Among our passengers were R. Hoffmann of Clausthal, P. Walden of Riga, G. Goldschmidt of Vienna, G. Komppa of Helsingfors, V. Kohlshuetter of Bern, M. Freund of Frankfurt-on-M., H. Wiebe of Berlin, E. Eblher of Heidelberg, F. Ehrlich of Breslau, A. Skita of Karlsruhe, A. v. Antropoff of Riga, E. Boernstein of Berlin, P. Heermann of Lichterfelde, H. Lange of Krefeld and C. G. Schwalbe of Eberswalde, so that besides mutual sociability and entertaining sports there was no lack of talking shop on the promenade deck.

At the outset, the organization in New York seemed to work very smoothly. Directly upon the arrival of the steamer at the pier and our release from the custom inspection, in which we were materially aided by American members who came to receive us under the guidance of V. Coblenz, we proceeded to Columbia University. Here, for many of us who had applied in advance, provision was made for free lodging in the University Dormitories. The journey to the University was taken on a steamer specially provided for us by one of the Committee and this journey along the Hudson afforded a complete and

<sup>1</sup> After writing this report, I received a copy of an address by Prof. Bernthsen of Mannheim on his impressions of America (*Chem. Ind.*, **36** (1912), 744; *Chem. Ztg.*, **36** (1912), 1329) to which I would refer all who are interested, as he supplements my experiences in regard to many matters. As there were no material differences between this address and my statements which follow, it was not necessary for me to make any alterations in my report.

surprisingly pleasant view of New York with its exceptionally pretty situation and of the everchanging beauties of the Hudson shores.

At the University we were at once ushered into the lecture room by the energetic Prof. Rassow, who was present with our American fellow members, without having any opportunity of visiting the lodgings provided for us. Here we listened to a lecture by Prof. Raschig of Ludwigshafen, on the tar-phenols<sup>1</sup> which was a veritable treat and made us forget all the worry concerning our lodgings which trouble, indeed, was saved for many.

I must give the preference to the manner employed in reading papers by the Germans. In Germany and in New York Germans, even with the manuscript before them, spoke freely and easily while American and Englishmen read in a wearisome monotone.

During the lecture our hand-baggage was left in an empty lecture hall which had been converted to a cloak room, but at the next address by a German-American member the new arrivals sought their lodgings in Hartley Hall and elsewhere and were thus soon made acquainted with another activity of the Congress, the providing of the indispensable dwelling and sleeping quarters. As the college vacation lasts until the 14th of September we had at our disposal the students' rooms in the dormitory building about ten stories high. In the most provident way our baggage labels had been sent to us in Germany bearing the directions "New York, Columbia University, Hartley Hall, Room No. —." The dormitories have a wonderful and beautifully arranged entrance, a well-conducted Information Bureau, an elevator with a colored attendant, and an ice-water cooler with individual sanitary cups; these were the only provisions made in the dormitories for the inner man and on account of the hot weather were much used. The apartments furnished adequate comfort, avoiding luxury, and meals could be had at reasonable prices on the University grounds, either in the pleasant Faculty Club with its reading and card-rooms or in the University Commons. The Committee on Organization deserves hearty thanks for thus solving the problem of housing the foreign members and for looking after those content with the simplicity of the students' quarters as well as those who preferred the neighborhood of the University because of its location, removed somewhat from the city and rendered attractive by its good air, its gardens and playgrounds. Even the ever genial and amiable President of the next Congress, Prof. P. Walden of Riga and his Baltic confrères as well as the Head of the German Central Committee, made use of the admirable arrangements of the dormitories.

About noon of the first day we took our first American "lunch" at Claremont Inn which has such a commanding and beautiful situation on the bank of the Hudson. It was here perhaps that ice-cold drinks and strange food, together with the great heat, were the cause of the gastric and intestinal catarrh which was later so common and so violent a complaint among the European members.

In the afternoon, under the kindly guidance of American members, I visited the fine Club House of The Chemists' Club of New York, which is indeed a model institution, both in satisfying the needs of the scientific inquirer and in the hospitable aspect of its quarters. The building is narrow but ten stories high and combines on the different floors, lecture, library and social rooms, all most appropriately designed for their use and purpose. Besides these are numerous bed-rooms for the use of members of the Club. As my fellow-traveler, Dr. Hans Alexander, has said lately in his charming paper<sup>2</sup> on his American trip, Berlin could be congratulated if it had such an institution for the numerous active representatives of applied chemistry in and about the city.

<sup>1</sup> *Chem. Ztg.*, **36** (1912), 1069.

<sup>2</sup> Read at Berlin, November 19, 1912.



On the evening of the first day, a German Kommerz was held in Arion Hall on Park Avenue. This was admirably conducted in a masterly way by Dr. H. Schweitzer of New York. There was an excellent burlesque—"Bierspiel 909," good Milwaukee beer and the best of good nature prevailed. The representatives of various nations made addresses, that of Engler of Karlsruhe being especially humorous, so that all the members enjoyed themselves thoroughly and became more and more intimately acquainted.

The journey to Washington was made in special trains on the 3rd of September to attend the Official Opening of the Congress. For this trip the Committee had secured a considerable reduction of fare. Occasion was offered here for the members to know each other better and many interesting relations were established with our American colleagues. Near me on the way down sat Dr. Takamine of New York with whom I took my first American meal in a dining car. He is the discoverer of the process of preparing adrenalin which is made according to his directions in the pharmaceutical factory of Parke, Davis & Co. in Detroit, which we later visited. After the hospitable American fashion, following a short acquaintance, he asked me to come to see him and I regret that lack of time gave me no opportunity to accept his friendly invitation.

In Washington, however, a distinct halt in the working of the organization took place. President Taft was to open the Congress at 11 o'clock in the morning of the 4th of September and afterwards receive the members at a lawn party at the White House. However, the members of the Congress were not informed where headquarters were established, nor were admittance cards could be had for the Opening or for the various other places of interest. It was only by accident that the place of registration in the Hotel New Willard was discovered and for a long time the members were kept waiting to go through unnecessarily delaying formalities which subjected them to considerable difficulties. Finally, however, forms were dispensed with and the impatient guests were at last promptly registered.

The Congress was opened in the Continental Museum by the president, Dr. Nichols, who in a humorous vein acted as the representative of the other president, Mr. Taft, who was unfortunately unable to attend on account of a sprained ankle. After this were speeches by Dr. Edward W. Morley, Honorary President of the Congress, and Dr. Nichols who represented the 6000 American members, companies, works, etc.

Representatives of the various nations then spoke in order, Germany being represented by von Buchka of Berlin, and Engler of Karlsruhe; Austria by Wegscheider and Strohmer of Vienna; Russia by Walden of Riga; England by Ramsay of London; France by Lindet; Italy by Ciamician; and Norway by S. Eyde.<sup>1</sup> Most of the addresses reflected the nationality and race of the speakers in unmistakable manner. Engler of Karlsruhe, who appeared as the second representative of Germany, spoke in his well known original way of the constantly growing competitive industry—Brewing—in which Germany and America are great rivals; his address was greeted with great applause. After each speech the national air of the speaker's country was played. In the afternoon President Taft received us in the White House looking well and hearty. He delivered an address on the important reciprocal influence of Chemistry upon the Industries with special reference to the American Patent situation and he pleaded for a better protection of the inventor. After this refreshments were served on the beautiful lawn of the White House gardens which was a welcome arrangement on account of the severe heat. The President was seated and gave each a hearty handshake as he passed, saying at least "I am very glad to see you." All that desired to speak at greater length found a willing listener. In the evening there was a reception in the new National Museum at the in-

vention of the Smithsonian Institution. The Museum has a very interesting ethnological collection and a notable picture gallery. The reception was somewhat dry for the German palate, especially considering the oppressive heat, but despite their unslaked thirst, the younger members danced, surrounded by stuffed giraffes, the skeletons of saurians and similar animals—distinctly American. The next afternoon we visited the very noteworthy laboratories of the Bureau of Standards, the Carnegie Institute and the Geological Survey; in each of these the Director or his assistants received us in the most cordial way and gave us all the information we requested. The employment of electricity in heating, stirring, etc., is perhaps nowhere so advanced as in the American laboratories, as we had occasion to observe later in the Bureau of Mines in Pittsburgh and in the various works-laboratories. The Bureau of Standards has most appropriately arranged chemical and physical laboratories and combines somewhat the functions of the Royal Testing Station and the Physical and Technical Institute in Berlin. Not only are materials tested with respect to their physical and chemical character, but thermometers and optical instruments are calibrated and standards for heat, weight, optical and electrical measurements are also fixed. I was pleased to note, although contrary to my previous impressions, that the metric system is employed in all the investigations and publications of this Bureau. In the Carnegie Institute under the excellent guidance of Dr. Arthur L. Day (who is not to be confused with the esteemed director of the Geological Survey who is in charge of petroleum statistics and technical petroleum questions), the work consists mainly of geological experimental examinations upon the alteration which rocks undergo under the influence of extremely high temperatures and pressures.

I need not speak of the various architectural points of attraction in and about the Capitol city which were visited in so far as the short time at our disposal permitted us. Unfortunately the heat had increased in the meantime to almost 100° F. Washington is on the parallel of Palermo and is correspondingly higher than New York which lies only on the parallel of Naples. When we returned to New York on the 5th of September, the heat had not diminished and on this account many of the members living at the University, gathered at our "bar," the soda fountain on Amsterdam Avenue in the rear of the University, and there in a long row at the counter joyfully drew through straws the refreshing but not altogether harmless drinks which somewhat revived our drooping spirits. It is really wonderful what the Americans drink in the way of lemon, orange, and sarsaparilla extracts at nearly all bars and drug stores; naturally the preparation of these extracts has gradually developed into a considerable industry.

The next morning the scientific treatises were scheduled to begin. It was said that this Congress would introduce a distinct novelty. All articles sent in up to the 5th of August, 1912, provided the authors furnished two copies and two short extracts, were to be printed before the Congress and furnished to all participants. However, on the journey to New York and also in Washington, I had heard much of the rejection of numerous articles written by noteworthy German members and many harsh criticisms were directed against the management. Of course the Congress had for a long time before thoroughly acquainted the members through its printed notices that only those articles would be received which introduced something distinctly novel. This, considering the large mass of articles presented at an international congress, is a praiseworthy precaution but it puts upon the management a considerable responsibility to the authors whose articles are rejected, and especially when the authors have devoted so much time, trouble and expense to matters of importance to their countrymen. It cannot be denied that many instances occurred in which papers were accepted or rejected without proper argument and

<sup>1</sup> See also *Chem. Ztg.* 36 (1913), 1069.

the part of those in charge of the New York Congress.<sup>1</sup> It was not to be wondered then, that at last one of our most valued German savants in his no longer controllable agitation thundered his opinion and that of his German colleagues in no uncertain terms in speaking to the manager of the Congress who was charged with the disposition of the papers. Of course the rejection or acceptance of the communications did not rest wholly with the manager but was committed to the Publication Committee of each section, made up entirely of American members. This plan does not seem to have worked well and it would be better to leave the disposition of the papers in the hands of an international committee and to demand an earlier submission of the communications. I may add that my own experience was unfortunate when I wished for report purposes to acquaint myself with the scientific articles which had been sent to some of the sections. My efforts were opposed in the most unfriendly way by the manager who insisted upon reserving to himself all rights of deciding such matters. The woman in charge of the office was very willing to grant my request to make abstracts of those contributions and discussions which had been handed in but not yet printed. Some of these articles I was not able to hear or could not follow on account of difficulties with the language. The manager, however, refused my request with the harsh order "You can print nothing over there (in Germany) until everything is published here." A bureaucratic European could scarcely have acted in a more dictatorial manner than he did with the consciousness of unrestricted power in his decisions on many matters of moment while no doubt he was of considerable service to the success of the Congress in other respects.

A pleasing novelty introduced in this Congress was the presentation to the members of twenty-four volumes of the Original Communications before the opening of the Congress. This satisfaction was somewhat modified by the fact that they were not distributed until just at the beginning of the session and that the members had the burden of their impressive bulk to carry off while they might have been sent before the members had started on their long trip. This was done with the articles communicated to the International Congress for Testing Materials which held its sessions in New York coincidental with our own. Only a small number of members took part in the discussions or were prepared to do so. It could hardly be expected to be otherwise when one considers the many attractions and diversions of the city, the oppressive heat that prevailed and the merely casual interest of many of the auditors who lingered at the lectures.

A novel American practice was employed for recording the communications of the Congress. It was intended to have all the discussions of the lecture room taken down by dictaphone; each one who took part in the discussion was to correct the record on the following morning, but as often happens this fine novelty worked poorly and many of the discussions became unintelligible. Later on the arrangements for the use of the dictaphone were so perfected that it is supposed to have worked much better. It would have been better to depend on the reliable stenographic method for recording the discussions.

Some meetings had to be abandoned entirely, e. g., those of Section V which shortly following its opening closed on account of the barrack-like quarters with only a temporary roof which economy had made necessary. Here the intense heat made it impossible to hold the meeting and any transactions were impossible. The faults here described are referred to in order that later Congresses may not repeat them. The insistence on them here does not, in any way, diminish our appreciation of the extreme care and trouble, often at great personal sacrifice that was taken by the leaders in the Congress. Our American

colleagues tried to make our stay in New York extremely pleasant, both from the scientific and personal standpoint; they assisted us in every way, both there and on the various technical trips that were taken. This we can never forget and it affords a firm basis for the cultivation of many friendships. Special thanks must be given for my own part, to the respective section chairmen Dr. D. T. Day, Dr. F. Schniewind, Dr. M. H. Ittner and Dr. G. Bumcke, for the special information furnished me.

Among the many addresses I heard were the following: Engler<sup>1</sup> on the formation of asphalt; Bergius of Hanover on the formation of coal from peat under the influence of high pressure and temperature; Sadtler of Philadelphia on the direct estimation of oxygen in organic bodies by the action of hydrogen in the presence of iron as a catalyst; A. M. Nastjukow<sup>2</sup> of Moscow on studies of the constitution of lubricating oils, as a result of the formolth reaction; P. H. Conradson<sup>3</sup> of Franklin, Pa., on the undesirable chemical changes brought about on lubricating oil in turbine bearings, etc., by water, different metals and electric currents. The last mentioned address was given before section Vc, "Fuels and Asphalts," and on account of its great interest to the petroleum industry was repeated at the meeting of the International Petroleum Commission held in The Chemists' Club on the 7th of September under the direction of Irving C. Allen. Of those lectures which were noteworthy both because of the eminence of their authors and because of general interest in their subjects, the following may be mentioned: Berntsen of Ludwigshafen-Mannheim<sup>4</sup> spoke on the synthetic production of ammonia, and after an erudite historical survey of the subject, described the development of that field of research which has been holding the attention of chemists for a long time, i. e., the development of the newest and now technically accomplished synthesis of ammonia from atmospheric nitrogen and hydrogen under the influence of high pressure and temperatures and with the assistance of catalysts, as based on the ideas and experiments of F. Haber of Karlsruhe (now of Berlin).<sup>5</sup>

A lecture by Eyde on the utilization of atmospheric nitrogen in other ways, received much approval, not so much by reason of its novelty as on account of the excellent illustrations shown.<sup>6</sup> G. Ciamician<sup>6</sup> of Bologna, the master of scientific photochemistry, showed in his lecture (delivered in Italian) on the "Photochemistry of the Future," numerous characteristic instances taken both from nature and organic synthetic chemistry, of how the low temperature light rays of the sun induce chemical processes in plants and in chemical organic bodies.

Although the lecture was not scheduled, Perkin, by invitation of the Americans, described his work on the synthesis of rubber<sup>6</sup> and it was extremely interesting to note that the lecturer showed the specimen originally made by Tilden, and that apparently the Americans were anxious to emphasize the work of Tilden, which to this day is of purely theoretical value as opposed to the great and decided success of Germany in the synthesis of technically useful rubber. Any one who knows the German chemical literature on the question of rubber syntheses has been thoroughly acquainted with Tilden's researches on the synthesis of rubber for a long time. Another address by Perkin was on the subject of the fireproofing of cotton fabrics<sup>6</sup> by means of sodium stannate and ammonium sulfate; his exposition of the method and the numerous experiments shown won for him much applause.

Gabriel Bertrand of Paris, Perkin of Manchester, Duisberg of Leverkusen and Ciamician of Bologna constituted the four

<sup>1</sup> *Chem. Ztg.*, **36** (1912), 1188.

<sup>2</sup> *Ibid.*, **36** (1912), 1220.

<sup>3</sup> *Ibid.*, **36** (1912), 1133.

<sup>4</sup> *Ibid.*, **36** (1912), 1132.

<sup>5</sup> *Ibid.*, **36** (1912), 1131.

<sup>6</sup> *Ibid.*, **36** (1912), 1139.

<sup>1</sup> See also H. Grossmann, *Chem. Ind.*, **36** (1912), 629.



speakers invited to deliver addresses. Bertrand spoke on the surprisingly great effect of small quantities of chemical substances in biology, especially in agriculture.<sup>1</sup> In the general assembly on the 9th of September held in the large Assembly Hall of the beautiful College of the City of New York, C. Duisberg gave his lecture on the "Latest Achievements and Problems of the Chemical Industry";<sup>2</sup> this received general and noisy applause on account of the masterly presentation as well as the magnificent illustration and experiments and the sterling quality of its contents. Of much interest of those engaged in the petroleum industry was the fact mentioned in the lecture that the benzene works in Reisholz near Dusseldorf are isolating aromatic hydrocarbons from Borneo petroleum.

As I was invited to visit the large refineries of the Standard Oil Co. in Bayonne, N. J., near New York and the Glycerin Works of Marx & Rawolle in Brooklyn, I was forced to be absent from some of the important lectures. In addition to this, like a good many of my colleagues, I was more than once indisposed and thus also prevented from attending at times, and had to be satisfied with reading them after the Congress had closed. When I add to what I (and others possibly more so) have derived from hearing the lectures, the value of the active discussion and what we learned from the visits to factories and laboratories I must give expression to what I heard on all sides, namely, that the Congress must be pronounced a distinct success and I am sure each member on either side of the ocean is of a similar opinion. Even now in looking back upon the Congress an especial attraction seems to hover about the city of New York and each one of us feels that if not an actual, he is an academic citizen of the proud Metropolis.

It was to this decided success of the Congress that the refusal of the suggestion to have it at longer intervals was due. The German members, somewhat tired of the duties of the Congress, made the proposition that it should be held only every five years. It would undoubtedly be much better if the number of the sections<sup>3</sup> were diminished—in New York there were 24—when one considers what demands the activities of the meeting make upon the participants and a much more distinct and generally recognized success would certainly be attained if a smaller number of papers were read. In Berlin in 1909 at the 5th International Congress there were 479 communications. In Rome 658, in London 985 but in New York 1000 articles were sent in, 300 contributed by Americans alone. It would be well then, to diminish, in some degree, this trouble to the organization and simplify the question of eligibility of the members. A great deal of the vexation during the Congress was caused by the difficulties placed in the way of the members in this latter matter.

But the questions touched here also have a serious side. The excess of scientific material furnished lowers the plane and lessens the significance of the Congress and furnishes too great a field for those who visit it for the social and other non-scientific purposes. Hereby the opponents of such congresses which are of so great an importance to the progress of science and the strengthening of the international relations are unnecessarily given material for criticism and many earnest colleagues turn to special Congresses smaller in their scope and extent. It must be said, however, to the advantage of New York that the social activities did not in any way prejudice the scientific value of the meeting. A social feature of the Congress well worthy of imitation and especially enjoyed by the ladies, was the daily 5 o'clock informal tea held on the lawn of the College of the City of New York. These were most enjoyable, both because of their social simplicity and the refreshment which they afforded.

Of the two receptions held in New York, I was able to attend

only that at the Chemists' Club. This function was rendered somewhat unpleasant on account of the intense heat and the large number of participants who gathered in the quarters which were too small for the 1500 in attendance. The official dinner of the Congress took place in the most luxurious hotel in New York, the Waldorf-Astoria, and was exceptionally well conducted and interesting. Care should be taken, however, lest this function of the International Congress become entirely too exclusive, by reason of its expensive character. Many members in ordinary circumstances and the younger members not yet richly endowed with this world's goods, are prevented from attending these affairs. One of the most attractive features of the meeting was the trip up the Hudson on Sunday, September 8th, for which we had fine weather although it was rather hot. During the hours of leisure or interruption in the work of the Congress, I visited Central Park, which gave ample opportunity for recreation, and the zoological and botanical gardens furnished a good means of studying the flora and the fauna of the country.

Unfortunately, a few days after the close of the Congress, when most of us had started on the technical trips, a shadow fell over the activities of the Congress. Geheimrat Wiebe<sup>4</sup> of Berlin died on the 18th of September of cerebral paralysis. He was a friend of many of the members of the Congress and will long be remembered by them. The incident was especially sad to me as I had parted from him at our hotel on the morning of September 15th not expecting anything so lamentable. Although a physicist, he had earlier pursued chemical studies which gave him a lively interest in questions of chemical apparatus and other related subjects and had contributed interesting communications to the work of the Congress under the section "Fuels and Asphalt" and to the International Petroleum Commission.

#### Impressions of Industrial Plants

The following is a description of the industrial plants visited by me in company with my friend Dr. Hans Alexander of Berlin, and his brother. These plants, in the neighborhood of New York, were inspected by us after the close of the Congress during a journey lasting about 2½ weeks. On account of the fatigue consequent upon the Congress we had decided not to take part in one of the longer official trips and although strangers in the land we traveled according to our own whims. By a practical division of labor we simplified the responsibilities of the trip. My companions concerned themselves with the somewhat complicated arrangements of the tour which included Atlantic City, Philadelphia, Baltimore, Pittsburgh, Chicago, Detroit, Niagara Falls, Toronto, the St. Lawrence River, Montreal, the White Mountains, Boston and New York. I looked after the arrangements for the visits to places of technical interest. Our journey was a pleasant one from first to last, barring a delay of six hours caused by a railroad wreck near Pittsburgh and a collision of our carriage with an automobile in Montreal in which some glass and one of our trunks were broken.

Our first stopping place completely refreshed us after the labors of the Congress. This was the beautiful seashore resort, Atlantic City. Its long piers with their roomy pavilions, the fairy-like illuminations in the evening and its numerous opportunities for recreation and pleasure, astonished me as well as the many interesting features of the city. I visited the great steel and iron works of Chicago and the pharmaceutical works of the Wyeth & Co. in Philadelphia, the largest chemical factory in Detroit. In visiting the plants of the Standard Oil Co. and its branch concerns an introductory letter which I owe to Dr. Riedemann of the German American Petroleum Co. was of great service to me and opened the doors of the refineries. I had made in Berlin. My chief interest was in the refining of petro-

<sup>1</sup> *Chem. Ztg.*, **36** (1912), 1130.

<sup>2</sup> *Ibid.*, **36** (1912), 1000.

<sup>3</sup> *Trans. Roy. Soc. Edin.*, **36** (1906), 1000.

<sup>4</sup> *Ibid.*, **36** (1906), 1000.



Jeum and if I devote a large space to the subject it is because I can presume, since the petroleum question is now such an important matter in our national politics, that a wider circle of readers is desirous of becoming acquainted with the methods employed in American practice.

The Coal-Tar Industry in America is really limited to the production of light and heavy crude distillates of the lower and higher phenols, creosote, naphthalene, anthracene oil and pitches only, while more advanced products and dyestuffs can scarcely be said to be produced. The same holds true for the Canadian coal-tar industry. The considerable pamphlet comprising the communications to Section IV of the Congress, "Aniline Colors and Dyestuffs," is eloquent of the local situation. The so-called "coal-tar trip," which was taken by 23 chemists employed either in German dyestuff works or in allied industries,<sup>1</sup> owes its name not to the objective point of the trip but rather to the character of the activities pursued by the tourists when at home.

#### 1. THE PETROLEUM INDUSTRY

According to the statistics gathered by D. T. Day<sup>2</sup> the world's production of petroleum has again very largely increased in the last five years in all those countries coming into consideration, with the exception of slight variations in Galicia and Japan. In 1907, 35 million tons were produced while in 1911 the output had grown to forty-six and a half million tons, an increase of about one-third in the world's production, and this proportion was maintained when we consider the U. S. production alone, whereas in Mexico, in a similar period, the production had become thirteen times greater. Of this forty-six and a half million tons of raw petroleum, the U. S. alone furnishes 29.4 and Mexico 5.9 million tons, the two countries together thus producing about two-thirds of the total output. Galicia and Roumania produce about one and a half million tons per year. The production of petroleum in the U. S. in the last decade has shifted gradually more and more to the West, two-fifths of the American field being located in California. The Standard Oil Co., which was dissolved lately into a large number of independent subsidiary companies, buys and refines the greater part of the raw petroleum obtained in the U. S. but actually develops, on its own account, but few of the sources of raw oil. Not much more than 25% of its supplies come from these privately controlled sources. The rest is bought from the pipe-line companies whose tanks often adjoin the oil works or from the smaller producers. However, since most of the pipe lines are owned by the Standard Oil Co. it naturally exerts immense influence on the raw oil market. It may thus be assumed, and the belief corresponds to information otherwise obtained, that the Standard Oil Co. does not regard the actual extraction of the oil from the earth as a business attractive to investment at the present time. During my somewhat short stay in the United States I visited a number of the larger refineries in the northeastern states. These take up a considerable area, so much so, that in my inspection of the Bayonne works, to which I devoted a half day, I could scarcely see all of the plant although I availed myself of an automobile which is always available for the use of the Works. As I later visited a large number of other refineries and excluded any examination of that part of their installations which I had previously seen in other plants, I believe that the following accounts give a fairly good survey of the methods employed in oil refining. Before entering upon the description of the plants I must not omit to express my appreciation for the extraordinary courtesy and kindness with which all my requests for desirable information were met, as well as the freedom and thoroughness with which later information was supplied by correspondence.

1. THE BAYONNE REFINERY—The Bayonne Refinery, which is just across from New York in the New Jersey group of Standard

Oil Works, is probably the second largest in the world. It was the first oil works in the East which I had an opportunity of visiting during the Congress on the 12th of September. The director, Mr. Gifford, and the head chemists, Messrs. Cobbs & Robinson, conducted me about the works, which are separated from New York by the Hudson and lie southwest of the city in Bayonne, which is situated on a small strip of land lying between Newark Bay and the upper bay. Every day the plant works up about 40,000 barrels of raw oil, producing benzine, light oil, middle oils, paraffin and paraffin oil. This is annually more than the total raw petroleum production of Galicia or Roumania. For its raw material the Bayonne works chiefly employ Illinois oil or that from the Ohio and Pennsylvania fields. The oil naturally does not contain sufficient light petroleum and benzine to meet the needs of the market and therefore in the first distillation it is decomposed ("cracked") so that the heavier portions are converted into the lighter illuminating oil distillates. The distillation is conducted without vacuum or steam. To cause the greatest possible decomposition, the distillate, as it rises from large horizontally arranged cylindrical stills, is led into a high column filled with loosely packed stone where the vapors are exposed to a very large surface; they are then led into a dephlegmator tower made up of numerous vertical iron tubes and finally to the condenser. Thus in both columns, by reason of the large surface to which the oil is exposed and of the air condensation, a considerable proportion of the heavier vapors is condensed and run back again into the stills where they suffer a renewed decomposition into lighter distillates. This method of working up petroleum, which is characteristic of the northeastern states, is carried as far as is practicable to produce a good burning illuminating oil and a benzine of high boiling point. It is adapted to oils not rich in constituents of high lubricating value.

As in all petroleum refineries, distillates of various boiling points and specific weights are led through various separating tubes, and according to their variation in specific gravity as determined by rapid test, are conducted into various reservoirs adapted to receive them. The stills are built in, in so far as the heating allows, but are not, as is the German custom, housed in special buildings. They are heated in common, a cheap rather small sized anthracite coal being employed. Oil heating is too expensive in this locality on account of the distance from the wells. After the benzine and illuminating oil fractions have been distilled off, the middle oils and paraffin remain. These are finally driven off until nothing but coke remains. This last product is employed as in Europe in manufacturing electrodes for arc lamps. The so-called paraffin fraction is treated with a brine solution brought to a low temperature by a battery of ammonia ice machines; the paraffin is thus brought to a salve-like consistency, and is then taken to a chilling room and pressed between cloths in very large horizontal filter presses. The chilling of the oils by brine takes place in horizontal cylindrical drums placed concentrically in cylinders of still larger dimension; the brine solution flows in the surrounding space while the oil is slowly conveyed in the opposite direction by a series of propellers which are revolved by a central axle. About five such chilling drums in which the oils are brought down about 5° C. constitute a battery. This patented cooling-installation is made by the firm of S. L. Moore Sons Co. of Elizabeth, N. J. The paraffin cake left after pressing is then freed of its last traces of oil by the Scotch Sweating Process. This process (also in use in Austria and Roumania) runs the molten paraffin into shallow pans and after solidification gradually heats the pans and the space about them by means of steam coils, until the excess of oil is sweated out and runs away through appropriately arranged pipes. The remaining paraffin is then treated with concentrated sulfuric acid and appropriate bleaching compounds such as ferricyanide residues, until it has the de-

<sup>1</sup> See also the above mentioned report of Bernthsen.

<sup>2</sup> Report of the U. S. Geol. Surv. on Petroleum 8 (1912), 144.

sired color and a sufficiently high melting point. The great output of the Bayonne refineries demands sweat chambers somewhat different from those employed in European practice. Instead of a large number of small pans the paraffin is sweated in very large ones arranged one above another. They are about 30 m. long, 5 to 6 m. wide and 15 cm. deep and take up nearly the entire length and breadth of the sweating chamber. Fig. 1 shows one of the twelve sweat rooms in the plant's installation. The oil residues from the paraffin are employed as light liquid lubricating oils after being subjected to treatment in special stills by the so-called continuous distillation<sup>1</sup> in which a small vacuum is employed and superheated steam is admitted. Oils of high viscosity, *i. e.*, heavy lubricants and cylinder oils, are not made in the Bayonne plant because in the cracking process employed, the heavier and viscous oils are decomposed into the lighter fractions.

The clearing of the oils, as well as of that recovered from the paraffin, is done by filtration through coarse-grained Fuller's earth. Ohio oil which is quite rich in sulfur must be desulfurized before it can be employed for illumination. For this, the Frasch process, named after its inventor who devised it twenty years ago, is still employed at Bayonne. The oil is heated, while being steadily stirred and agitated with current

of carbon disulfide. A hood at one side of the tank can be turned automatically and the next edge presented. This is done until the can is completed, when it is automatically delivered at the end of the apparatus.

As far as size is concerned, the nearest approach of the European refineries to this large great American plant is that of Steaua Romana in Campina, Roumania, which produces three-quarters of a million tons, or at least half the production of the country. However, I may say that the European plants, for example that in the Vacuum Oil plant in London, working under American control, is much more satisfactory from the standpoint of the economy of labor. A heavy and found in the American refineries anything like the economic employment of the heat from the distillation vapors and from the distillation residues which I have noted in Austria, Roumania and at the Vacuum Oil plant, where this heat is employed in preheating the raw oil thus effecting distinct economy.

The directors of the American plants, while aware of this difference in European practice, are not inclined to consider the question of economy of labor when the great economy and efficiency of their raw material is considered.

THE STANDARD OIL CO. OF PHILADELPHIA. The Philadelphia plant is the largest of the group belonging to this



Fig. 1

oxide and the greater part of the sulfur combines with the oxide. The copper oxide slime thus produced naturally contains a great deal of copper sulfide, and is recovered from the desulfured oil in filter presses and then regenerated by roasting, after which it is again ready for use. The waste gases, which have escaped all the methods employed for their condensation, are used in driving large gas engines which are coupled with dynamos. Nor does this represent the sole employment of these waste gases as the gases are used also in the can works. A large number of these cans have to be made and are shaped with extraordinary rapidity on automatic machines. The soldering baths through which the edges of the tin cans are drawn, are heated by the waste gases. The cans hold about a gallon and are used chiefly for shipping illuminating oil for the far East. They are made by the hundreds of thousands daily in the works; after they come from the shop cut out of the tin plate, they are shaped in proper form, brought to the steam-heated soldering bath and their edges soldered, the whole operation being

continuous. It works out about 3,000 bbls. of crude oil per day. (The other works are at Franklin and Pittsburgh.) The oil comes for the greater part from West Virginia, and is sent by a pipe line 300 to 400 miles long to the Philadelphia Refinery. The works lie at the dock and tank steamers take the product or the pipes to Europe and other countries. As one of its products is made for export trade, The Philadelphia works of the same company, which refines about 3,000 bbls. per day, is run only to supply the American market. The Franklin Refinery, handling 100,000 bbls. a day, is also chiefly run for the domestic market. The Philadelphia plant makes a light, white oil and a number of waxes, however, as well as the transmitted light, but does not produce kerosene. It produces all grades of kerosene, oils, vaseline, light and heavy machine oils, cylinder oils and coke.

In contrast to the Bayonne Refinery of the Standard Oil Co., this concern makes a specialty of the better grades of lubricating and refined oils, in addition to fuel distillates and kerosene. Here, as in the Bayonne Refinery, the crude oils are subjected to the usual series of treatments, but are "cracked" by catalytic action and then recombined, without the use of steam, the whole operation being carried out in the still. The steam and water for the production of kerosene are generated by distillation and, with the distillation, with direct steam, are separated, while the lighter fractions have been driven off, leaving the oil and about two per cent steam. In the next case, the

<sup>1</sup> In this process, which is also employed in the Vacuum process, the cans are arranged in terraced beds one another being distanced in height by, for instance, 15 cm., with each one the oil being run off each still to that that oil, after the removal of the lighter fractions, goes on to the next still, from one still to the following one, and so on, until the oil is in the final distillation still. Such a plant requires little cooling and much less steam than the ordinary use of the available heat.

distillates, as in the Bayonne Refinery, are redistilled. A greater part of the illuminating and lubricating oils are filtered through Fuller's earth. In the second case the horizontal stills which, like those in Bayonne, hold several thousand barrels of oil, are provided with wide outlet tubes through which the vapors can pass unhindered and promptly, thus avoiding decomposition. Further on, these vapors meet in a single leader. After the distillation of the heavy machine oils, cylinder oil remains in the still as a dark, fluid residue which, according to the desired viscosity or flash point, is further evaporated. The product, when filtered through Fuller's earth, is of a greenish color by direct sunlight but of a somewhat reddish cast when viewed by transmitted light; without filtering, it is a deep greenish black. The clearing of the oils with Fuller's earth is employed not only for cylinder oils but for many machine oils. The rather coarsely grained Fuller's earth is roasted in large rotating sheet-iron drums of about 5 ft. in diameter while the flames of a strong coal fire beat down upon the moving mass of Fuller's earth. The roasted earth is then treated in rotating drums upon which cold water is continually sprayed. The cooled material is then ready for clearing the lubricating oil. This is done in very large cylinders with conical bottoms upon which the earth is spread rather deeply, the oil being filtered while warm. This method of clarifying the oil is much employed in the Eastern American refineries as a substitute for the sulfuric acid and lye refining in the preparation of illuminating oil, machine and cylinder lubricants. An important advantage of the process is that it prevents considerable loss of oil which takes place by the acid treatment. When the earth has lost its power of clarification, by becoming charged with resinous matters, it may be regenerated by pressing out the oil at a high temperature, or by distilling off or extracting the oil by benzene; after evaporation of the benzene the oil-free earth is roasted as above described.

Brine from ice machines is used to chill the paraffin-bearing oils for recovery of the paraffin wax. These machines are, as in Bayonne, horizontal and concentric cylinders, the inner one in the Philadelphia plant having a diameter of 20 in. The latter is for the reception of the brine solution, the oil being placed in the outer cylinder, which has a breadth of 24 in. On the rotating oil-cylinders scrapers are placed which continuously detach the chilled oil as it solidifies. A few such cylinders through which the oil circulates in the opposite direction to the brine constitute a battery. The oil comes into the chilling cylinder at ordinary temperature, where it may be cooled as desired from 0° to 15° C. In all chilling machines working on similar principles it is necessary that the chilled oil and paraffin be promptly scraped from the cylinder.

According to information given me by the directors of the works the following methods of chilling are generally employed in the American plants: *First*, either a vertical cylinder 60 in. broad for the circulation of the oil stands in another cylinder of 64 in. breadth. In a concentric space between these two the chilled brine solution is pumped. In the oil cylinder a rotary scraper detaches the solidified oil from the walls. *Second*, a 6 in. tube for the circulation of oil is placed within an 8 in. pipe so that the brine circulates in the space between. In this case the device employed for scraping consists of an Archimedian screw which slowly moves forward in the oil. As in Bayonne, the paraffin mass is freed in the filter press from most of its oil and then brought into the sweating room where the remainder is removed.

Of course vaseline is also made at the Atlantic Refining plant in Philadelphia. For this purpose the crude oil adapted for its manufacture is chilled to such a degree that the vaseline-like amorphous paraffin separates. The supernatant oils are drawn off. The crude vaseline at the bottom is freed by distillation from any illuminating oil and is then clarified by filtration through bone-black or Fuller's earth. For the information ob-

tained and for my conduct about the works I am indebted to the Superintendent, Mr. W. M. Irish, and to the Chief Chemist, Dr. F. C. Robinson.

3. THE ATLANTIC REFINING CO., PITTSBURGH—This was the smallest plant of the Atlantic Refining Co. which I visited. It works up 3000 bbls. of crude oil daily, using the product of the Illinois and Pennsylvania fields. While this is small for an American plant, it corresponds closely to the total yearly supply of German petroleum or one-tenth that of Galicia, or about 1,000,000 bbls. The distillation of the crude oil takes place in this works in a different manner from that employed in the refineries which I visited earlier because the raw oil is rich in lubricants. Here the oil is distilled with steam only, in horizontal stills which are bricked in below but are open above or are covered only with sheet iron. The stills of 600 bbls. capacity have only one outlet tube. Those of 1000 bbls. capacity have several vapor outlet pipes which further on are united in a wider leader. All the stills in addition to the outlets have a vertical vapor tube provided with a valve for the inlet of steam under high pressure. The gases not condensable in the ordinary distillation are carried off by pumps, compressed and sold as light gasolene. The lubricating oils are clarified partly by Fuller's earth and partly by washing with sulfuric acid and lye in separate apparatus. The lighter oils are purified by the chemical method only. The paraffin-bearing oils are solidified by artificially cooled calcium chloride solutions, the paraffin brought to the filter press and then treated in large sweating rooms where it is deprived of the residual oil. In the chamber there are about 10 pans arranged one above another, being 33 × 10 ft. They are provided with a conical bottom and an outlet feed. The outlet tubes may be raised or lowered from without to the still. The plant prepares various grades of paraffin of a higher or a lower melting point according to the temperature which has been employed in the pressing. The low-melting grades are employed as illuminants, being substitutes for the liquid illuminating oils. In firing the steam boilers a rich bituminous coal is employed which costs \$1.45 per ton. The combustion was excellent when the fire was automatically regulated. The paraffin estimation is carried on in the works laboratory; 500 grams of the paraffin to be tested are pressed on a nine ton press between cloth and paper and the remaining dry cake is weighed. The viscosity is determined by a Saybolt apparatus and the flash point by the open Tagliabue tester.

North of Pittsburgh, in the neighborhood of Evergreen, I visited a few oil wells, but their daily output was quite small—only about one or two barrels. The oil obtained was a bright reddish yellow and on account of this quality sells at \$1.25 per barrel, so that even with such a small yield of oil it pays to conduct the work. This is also true of the old wells at Wietze, in Germany. In contrast to the proportionally high price of light colored oil, may be cited that of the dark California oil which sells for only 30 c. a barrel. On account of the low price of this grade the stills and boilers in the California works are often fired with the liquid residues of the oil distillation.

With regard to other points of technical interest visited in Pittsburgh, the time at our disposal was unfortunately limited by reason of the railroad accident earlier mentioned. Still we had time to visit the very interesting Carnegie Museum and to view the beautifully situated town which both nature and art contrived to render most picturesque in its location. The view of the town with its two rivers and the mountains of the Allegheny Ridge surrounding it is most impressive and beautiful in the evening when the fiery torches of the iron works light up the town.

4. THE STANDARD OIL CO., AT WHITING, near Chicago, has one of the greatest crude oil refineries and in many respects recalls the important European plants. It refines daily about 35,000 bbls. of crude oil and owes its present growth and develop-



ment chiefly to its experienced technical director, Dr. Burton, a former pupil of A. W. von Hofmann.

While in 1903 no oil had yet been produced in Illinois, 100,000 bbls. daily corresponding to a yearly production of  $4\frac{1}{2}$  million tons, are now produced. Besides the Illinois supply, oil from Kansas is also worked up in this refinery. This plant produces all the derivatives of the petroleum industry and in addition to those previously described it also makes bright cylinder oils. The crude oil is generally dark colored and belongs to the so-called paraffin-yielding oils. It comes in pipe lines from points as far as 500 miles distant. The raw oil is distilled in batteries of 10 stills each, the stills having a capacity of 1200 bbls.; six of these batteries are installed in the plant.

All of the crude oil is distilled without steam, in horizontal open stills with high reflux columns containing, however, no further division or stone filling. The heavy distillate is redistilled and gives at first, fuel-oil, then light and heavy machine oils, and in the residue automobile and machine oils. All of the oils are refined with sulfuric acid and lye or soda or ammonia; they are further clarified with Fuller's earth. Lubri-

cated oils are produced in the same way. The process is described by Dr. O. E. Bransky, the chemist at the works, seem to indicate that it should be possible to use the Fuller's earth 30 times without regeneration. The filtration of the oil through the Fuller's earth is conducted at a temperature ranging between 20° and 50° C., according to the consistency of the oil. The roasting of the fresh earth or of that to be regenerated is conducted as in the other works in long rotating drums made of thick sheet iron covered on the inside with masonry. The drums are fired with oil working on the reverberatory plan. The roasted earth drops from the drum in which it is heated into a cooling drum, whence it is brought by an elevator into large storage bins. From these bins it is carried by a belt and by moving belts to the large filter houses. After the earth has lost its power of clarifying it is extracted in the filtering cylinders with benzine. The benzine solutions are distilled with steam, the residue constituting a light or heavy dark machine oil. The numerous chimneys of the works discharge heavy black vapors which were avoided in the Pittsburgh plant by securing better combustion by automatic regulation of firing.

Of special interest are the very extensive paraffin and candle works of the plant. Elsewhere the pressed paraffin is treated by the Henderson process, being sweated by steam heating to recover the last traces of oil, but at Whiting the sweating of the paraffin takes place in tall tank-like cylinders, "sweating ovens" of 40,000 gallons capacity. Here the heating is done by gradually warmed water led up through numerous vertical tubes from below somewhat like the preheaters employed for the crude oil. The paraffin surrounds these tubes and the hot water passing through them brings it to the melting point and sweats out the oil which collects on the horizontal plates provided with outlet tubes. The paraffin treated is next melted, led into the top of the oven and then by the pumping in of cold water through the 12 inch vertical pipes, is brought to the solidification point. Warm water is then led into the tubes until the more easily melting paraffin has run off and the paraffin of higher melting point is left on the perforated plates. This is finally melted by steam, run off, and the oven charged anew. The advantage of this sweating process, in so far as I can make out, consists in demanding no special building and in the promptness with which the paraffin can be warmed by the water. The paraffin is kept in tanks similar to the ordinary oil tanks but provided with steam circulation for melting the material so that it may be readily put in or removed. In the candle factory which comprises three large moulding houses, candles of various sizes, color and form are made, for the most part mixed with stearin.

The plant also prepares lubricating and axle greases. The former are made from a mixture of rape-seed oil and tallow, or a mixture of lime and potash made up in a large battery of vats and treated with soap, the final product being led into tanks filled with mineral oil and mixed hot. The finished fat contains about 2 per cent of water and is packed in cases or wooden firkins. In the preparation of axle grease, the mineral oil is treated with acid resin oil and lime.

I must there thank Dr. Burton and Dr. O. E. Bransky for special information and for so kindly guiding me about the works.

I may add to the preceding report upon the American petroleum refineries of the East the following information which was gathered by Dr. E. Erlenbach who took the "long trip" of the Congress and visited the refineries and oil fields of the West and South.

There is a very poor oil, known as "black oil," which is a dark oil very poor in benzene. This is found in the large oil fields of Bakersfield, from which it is pumped in pipe lines to the Richmond Refinery of the Standard Oil Co., near San Francisco, and to Los Angeles, both of which cities lie on the coast. This oil is of the same kind as the "black oil" which is found

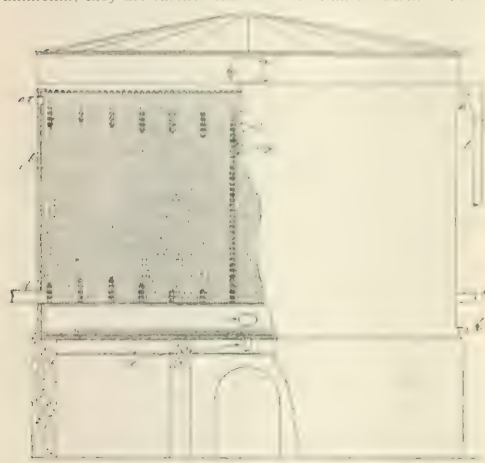


FIG. 1. A CROSS SECTION OF PARAFFIN SWEATING OVEN, THE OIL CO. OF INDIANA

- |                          |                       |
|--------------------------|-----------------------|
| a. delivery pipe for wax | g. steam jacket       |
| b. layer of asbestos     | h. steam pipe for wax |
| c. air space             | i. water jacket       |
| d. steam pipe            | j. perforated plates  |
| e. water pipe            |                       |
| f. delivery pipe for wax |                       |

cating oils, after this treatment with concentrated sulfuric acid, are washed with soda solution and then with water. Blomming oils are, after the acid treatment, washed with ammonia for the ammonia soaps thus formed are more easily soluble in water and more readily washed out. For refining the lighter paraffin oils 8 to 10 per cent of concentrated sulfuric acid is employed. In this plant vaseline is not prepared from the raw oil, but from the dark residue obtained on the redistillation of the heavy oils with steam. These residues are treated with benzene and then chilled considerably below 0° C. The solution is next siphoned off from the precipitate and after the removal of the benzene and filtration through Fuller's earth furnishes a bright cylinder oil. The precipitate, when freed from benzene and filtered through Fuller's earth or bone-black, gives a bright colored vaseline. The benzene recovered from the distillation of the crude oil is again rectified in stills provided with very simple dephlegmators, steam being employed in the redistillation. The filtration of the oil through Fuller's earth takes place in immense cylinders which hold a charge of 50 tons. The earth

and repumped. In the larger refinery of Richmond about 60,000 bbls. a day are worked up chiefly for illuminating oils, lubricating oils, tar and coke. The refining processes are quite as simple as those employed in the Eastern works, although a few departures from the Eastern practice must, of course, be expected on account of the nature of the material. Dr. Erlenbach was impressed with the more economic prosecution of the distillation in the European refineries by reason of the economy of heat employed and the fact that while these European installations demand a much more complicated apparatus they undoubtedly save in materials consumed.

Apart from the already referred to wastefulness of the Eastern Refineries in the matter of the economy of heat in distillation, the extraordinarily high wages for workmen employed in construction is sharply in contrast with European experience. According to Dr. Erlenbach, a mason received as high as \$7.00 per day and in San Francisco even as high as \$10. It is not at all unusual nor unnatural, when one considers his income, for a mason to go to and from his work in an automobile. In California the question of economy in the saving of heating material is not so important when one views the cost per calorie here, as it is in the Eastern part of the U. S. Raw oil can be had as low as 30 c. per barrel. On this account even the locomotives from Salt Lake City westward are arranged for oil firing, whereas from the Rocky Mts. to Salt Lake City they combine oils and coal firing. If one calculates the heating effect of the oil as about 10,000 calories per kilo, which is a million calories per 100 kilos, then the cost for these calories amounts to 30 cents, which, especially for large steam boiler installations or a great number of stills, effects a considerable economy, more especially when one considers the saving due to absence of ashes and smoke, and the small attention needed. A million calories, in Germany, costs for coal, which has only a heating effect of about 6,000 calories, nearly twice as much as this figure, not to speak of the corresponding increase in labor which is demanded in firing by coal, the saving of the disposal of the ashes, the smoke nuisance, and the correspondingly greater money stringency here. All these things must be taken into consideration when one comments upon the very simple installation of the American refinery.

The larger refinery in Richmond has such a demand for sulfuric acid for refining the dark oils rich in asphalt, that it has constructed its own sulfuric acid works using the contact system of the Vereinigte Chemische Fabriken of Mannheim. Refining with Fuller's earth is not adapted to these California oils which are so rich in asphalt. This plant uses silica slags as a contact substance. The ore used in the manufacture of sulfuric acid comes from the state of Washington. Since the California oil is extremely rich in aromatic bodies and asphalt the loss by refining with sulfuric acid is extraordinarily great. However, it is said that one of the by-products in the regeneration of the waste sludge acid is a material rich in xylol.

The tourists on the long trip then visited the field near Fort Worth, Texas, where oil is being obtained together with gypsum and sulfur. The edible fat plant of the Armour Co. was also seen there. The material is made by mixing animal fats with cottonseed oil which is a product of the same locality. In Louisiana the oil wells near Shreveport, in the great Caddo oil field, one of the largest oil fields of the southern states, were visited. This field, whose production last year was estimated at 1,000,000 tons, has been developed for 10 years and is giving annually an increasing yield. The oil is led to the refinery by pipe lines, but must be previously heated and also freed from dissolved gas which has a deleterious effect on the mains. The natural gas wells in the neighborhood of Shreveport proved very interesting. Their product is much employed in industry and even in the household. One of the gas wells was lit for the members of the Congress. Simultaneously with the gas, brine is

often thrown out from these wells and, as was the case here, the steam produced extinguishes the flame.

## II. ASPHALT AND ROOFING PAPER INDUSTRY

The numerous asphalt pavements which are laid in America are not made as in Germany, from a natural bituminous limestone (such as found in Sicily, the Abruzzi Mts., Limmer in Hanover, or Vorwohle in Brunswick), but are constructed of an artificial sand and asphalt mixture, owing to the lack of these naturally bituminous rocks in America. The mixture consists of sand and ground rock such as diabase, together with Trinidad or Bermuda asphalt and the addition of proper fluid materials such as petroleum residues, mineral oils, etc. The municipal authorities in the United States have stringent rules for the character of the methods employed in paving streets and in many localities the cities have their own asphalt plants.<sup>1</sup> According to H. Kayser, the American asphalt streets are laid more cheaply than those of Germany, and the German Trinidad Company is attempting to develop cement and sand asphalt pavements to do away with the necessity for the use of the bituminous limestone and thus avoid the heavy transportation costs of this article. Sand, as a rule, can be had in the neighborhood of the paving job quite cheaply. Further experience, however, must be had before it can be decided that this process can successfully compete with the methods already successfully employed in inland Germany. In New York rather stringent specifications are made for the supply of asphalt to prevent any material being employed for paving which has a considerable paraffin content. This impurity (the natural asphalt contains no paraffin) is introduced when the residues of the refining of petroleum are employed in asphalt manufacture, as these residues contain considerable paraffin. Experience has shown that much of this material renders the asphalt less elastic and resistant to changes of temperature.

The refinery of the Barber Asphalt Paving Co. is situated in Maurer, N. J., about an hour's journey south of New York City. I visited the works in company with its consulting chemist, Mr. Clifford Richardson, whose excellent researches on asphalt have rendered him widely known. On the way we passed through the new Baway Refinery of the Standard Oil Co., and had a chance of seeing, near the works, the immense pipe lines which here are above ground and which carry the crude oil from Oklahoma, 2000 miles away. The asphalt refineries at Maurer work up chiefly Trinidad-Bermuda—and other natural asphalts into a product adapted for paving purposes. The plant also impregnates wooden blocks and railroad ties with tar oils, asphalt oils, etc. The Trinidad asphalt is obtained from a lake on the island of Trinidad which annually produces 200,000 tons. For each ton gathered the company, which works up 80,000 tons at Maurer, pays to the English Government \$1.25, which tax constitutes the chief source of the income of the island. The crude asphalt contains 25 per cent mineral matter and 29 per cent water and is brought directly from the steamer to the melting pans, which are square in section and provided with iron steam coils to raise the material to a temperature of 150°-160° C. and thus free it as far as possible from gas and water. The asphalt then contains 56½ per cent carbon bisulfide-soluble bitumen and 36½ per cent mineral matter consisting chiefly of sand and clay. The asphalt is then brought into mixers for the addition of the oils which, according to the use of the material, bring it to the desired consistency. For this purpose mineral oils are used; for instance, the dark oil remaining after American oil has been treated with steam to remove the paraffin containing distillates and one specially adapted to this purpose is known as Trinidad crude oil and, after about 10 per cent of gasoline and illuminating oil have been driven off from it, it contains no available lubricating oil, but is a thick residue serving well in

<sup>1</sup> H. Kayser, "Report on Artificial Asphalt Pavements in America," *Techn. Gemeindeblatt*, 14 (1912), No. 12.



an asphalt mixture. The oil is brought directly to Maurer and worked up in the plant erected and managed by Dr. A. Summer in the manner above described. A simple distillation with steam in cylindrical stills is employed with no condensing column. The purified crude asphalt is sent out in barrels as paving material or it is mixed with 80 per cent ground rock, sand, and 10 per cent of powdered diabase which is found near the works and then in a pasty condition is moulded into blocks which are used for paving material.

The charging of the asphalt-oil mixture into the barrels is most rapidly done. The barrels are moved on an endless belt and are brought under the tank containing the mixture, which runs into the barrel through a tap, when, after the barrel is filled, the next one is promptly presented. Bermuda asphalt also is worked up in the plant. This contains about 95 per cent of pure bitumen and a production of 25,000 tons yearly is attained here. The Trinidad asphalt occurs in irregular grayish black lumps and comes to the works in its original condition while Bermuda asphalt is a soft material which is readily shoveled out of the storing sheds. The mixes made with this material are governed by this soft consistency.

As above remarked, railroad ties and wood paving blocks also are impregnated with tar and asphalt in various ways to suit the purchaser. The goods to be impregnated are placed in large horizontal cylinders with grated sides, and then this cylinder is brought into a larger one containing the impregnating material, pressure being used to aid the penetration which is conducted hot. The works laboratory is in charge of Mr. Clifford Richardson and his assistant, C. N. Forrest, and in it routine analyses of the asphalt content of the raw material and of the advanced products of the works are made, as well as the necessary physical tests. The laboratory is well supplied with publications relating to the industry and with practical apparatus for the chemical, physical and mechanical testing of asphalt. A simple test of the bitumen content of asphalt powder, or similar products, is conducted by taking 10 grams of the material, placing it in a tube about 5 mm. wide and 25 cm. high and then shaking with carbon bisulfide. It is then placed in a centrifuge and treated with fresh quantities of carbon bisulfide until the latter is no longer colored. The tube with the insoluble residue is then weighed. The solution is then evaporated and the ash of this residue determined. This figure is then added to the residue remaining in the tube and the difference between these combined figures and the mass of the material taken for the test gives the actual bitumen content of the original material. From the average of the bitumen content the ash content can be deduced. For more exact determinations of the bitumen a larger mass of material is placed in a paper shell in a metal extraction apparatus and treated with the solvent until the latter no longer runs colored into the extraction flask. The heating of the extractor is done by a wire spiral which is led into the flask and hangs down to the bottom, thus effecting a regular boiling of the solvent. The ash content of the extracted bitumen is deduced as before.

The melting points of asphalts which are not liquid at ordinary temperature are determined in an apparatus quite similar to the Kraemer-Sarnow<sup>1</sup> but the tube in which the material is held is of brass, conically shaped,  $\frac{3}{8}$  inch wide at the top,  $\frac{1}{4}$  inch at the bottom, and  $\frac{3}{4}$  inch long. In the lower part of the small tube is a screw joint which is used when it is employed in the determination of the viscosity of asphalt. To charge the tube it is placed on a brass plate which has been coated with mercury and then filled to the very top with the molten asphalt. After remaining in ice water at 5° C. for about 15 minutes, it is heated in the water bath until the asphalt runs from it. The temperature at which this takes place is the melting point. The viscosity determination for asphalt materials used in street paving can-

not be conducted on the Engler apparatus which is, however, adapted to the determination of the above fluid asphalts. On this account C. N. Forrest<sup>1</sup> has devised the apparatus which is employed by his company and in the New York Testing Laboratory as a standard for the determination of the viscosity of asphalt at 32.2° C. The material is filled into the small tube as above described, chilled in ice water, and then by the thread which it bears below the tube is screwed into a round aluminium cup. This is then heated in water, brought to 32.2° C., or any other standard temperature that may be selected. The time which elapses before the melting asphalt permits the entrance of the water into the cup and the consequent sinking of the tester gives the viscosity. According to the figures given for the test conducted at 32.2° C. on 17 samples of material of varying degrees of viscosity employed in paving, compared with the figures obtained on the Engler instrument, most of the materials do not flow from the Engler apparatus either at 25° or at 54.4°. Only at 121° C. were all samples (with the exception of one for which the Forrest apparatus gave a result of 69 minutes and 55 seconds) sufficiently liquid in the Engler apparatus that the interval of flowing could be determined. On this account the Engler apparatus is to be recommended for correspondingly high temperatures, *e. g.*, between 120° and 175° C. and the Forrest apparatus for tests made at 32.2° C. The ductility of the asphalt is determined in this laboratory by placing the material between two steel plates in a water bath at constant temperature and drawing these plates apart by a threaded spindle in a fixed number of seconds. The length of the threads of asphalt thus produced is a measure of the ductility of the material. In the Barber Asphalt Paving Co.'s plant, roofing paper is made in a manner quite similar to that employed in charging these materials with coal tar, the difference being that the material after a previous impregnation with an asphalt solution containing no tar is pressed between rotating steel cylinders. After this the chief process is the impregnation of the material by mechanically dipping it in a hot bath of a mixture of natural asphalt and oils and this is followed by pressing in these materials by passing it through rolls. The surface is then sprinkled with powdered gray limestone to prevent the adherence of the layers as the paper is rolled up.

#### III. SOAP, GLYCERIN AND OIL INDUSTRY

The soap works of Colgate & Co., in Jersey City, are directly at the exit from the Hudson Tunnel opposite the Jersey Central Railroad Station of New York City. I had a chance to visit the works under the friendly guidance of the chemical director, Dr. M. H. Ittner, and to witness the preparation of soap, caustic soda, and glycerin from the soap lye. As filling agents for some of the soaps, sodium silicate and sodium carbonate are employed. The crude fats, cottonseed oil, tallow, palm oil, etc., are purified in the works. The soap stock obtained by purification of the cotton seed oil with caustic soda consists of the free fatty acids in the form of soaps and the free neutral fats that are carried along with the dark colored materials of the raw oil. The soap stock is treated with dilute sulfuric acid to set free the combined fatty acids; these are then extracted, together with the neutral fats carried with them, from the acid waters and final treatment by the Twitchell process, with the so-called aromatic sulfonic acids, converts any neutral fats still retained into free fatty acids. The total fatty acids thus recovered are purified by distillation in superheated steam by the recognized method. The operations for the manufacture of soap are simple and well known. For the greater part neutral fats, and not fatty acids as is our present practice, are saponified. The saponification takes place in a large number of enormous vessels of cast-iron, each with an capacity with an inlet for direct steam. After saponification is complete the heating is continued with indirect steam. The large kettles are about 20 ft. in height. The

<sup>1</sup> Holde, "Untersuchung der Mineralasphalte," *B. W.*, 1904, 564, 565, 566.

<sup>2</sup> *Eng. News-Record*, 1907, 584.



soap separated after the addition of the salt is removed from the glycerin and salty layers and then converted into a homogeneous mass by the addition of water and heating with steam. After some days the so-called "nigger" has separated from the soap, which is then pumped into large square steel boxes with demountable sides and there solidified. After the removal of the walls the soap block is cut by wire in the usual manner into small pieces and then pressed into any shape desired for household or toilet uses. The wrapping is done by machine. Domestic soap to the amount of  $\frac{1}{2}$  million pounds daily is produced, as well as various sorts of toilet soaps, shaving soaps and sticks, tooth pastes, etc., and perfumes in large quantities by the use of the proper ingredients.

Glycerin is made in the works chiefly from the residual lyes obtained after the soap has formed. The glycerin is brought up to 98.5 per cent purity for chemical and pharmaceutical purposes and to from 99.1 per cent to 99.2 per cent for dynamite manufacture. The greater part of the alkali is neutralized in these lyes, which are then concentrated, whereupon most of the dissolved soap separates out and is removed. The further evaporation takes place under vacuum in vertical cast-iron vessels and is carried to the point where the increased concentration brings about the precipitation of salt and soap at the bottom of the vessel. Here lies a wide tap through which these materials may be removed as they settle. A large horizontal vessel lies below to receive this discharge. The stills are also provided with inlets for the charging of further quantities of the material to be concentrated. In these vacuum stills the concen-

tration of the glycerin is brought up to about 75 per cent. The glycerin is then distilled with superheated steam in vertical stills and the vapors are led through a row of wide pipes which act as an air-cooled condenser, and then finally into a water cooler. The condensed matter from the air coolers is the pure glycerin while the steam condenses for the greater part on the water cooler. Since the glycerin recovered in soap manufacture is not always sufficient to meet the demands of this concern's customers, it is frequently forced to buy crude glycerin. The factory, in addition to its soap and glycerin plant, refines oils and fats and is said to have 50,000 customers.

The largest cotton seed oil works of the U. S. (which, however I did not visit) is that of the Proctor and Gamble Co. in Cincinnati with a capital of \$50,000,000. It has also a branch works in Staten Island near New York and in addition to cotton seed oil and soap, it makes candles. This firm is said to have bought from the firm Crossfield Sons, Warrington, England, the license to employ the oil hydrogenation process of W. Norman and to have started on this new industry with considerable activity. The long trip of the Congress included in its path many large cotton seed oil plants. For example, those at

Forth Worth, Shreveport, Atlanta and Charlotte. Such plants are numerous in the U. S., owing to the importance of the cotton industry. The oil cake remaining after the expression of the oil is used both as a cattle food and fertilizer; in the latter instance it is usually employed mixed with other artificial fertilizers.

The method of refining cotton seed oil shown in Charlotte consists in treating the material with lye, whereby the coloring matter of the oil is taken up by the precipitated soap stock, "black grease." The thus clarified oil is further decolorized with Fuller's earth and is then adapted for use in cooking, etc.

On the invitation of Dr. A. C. Langmuir I visited the glycerin factory of Marx and Rawolle in Brooklyn of which he is the director. This is one of the largest works in the world with a production of about 8000 tons yearly. The chief supply of raw material is from soap lyes, but the glycerin-bearing water of the Twitchell Process which, being an American process, is commonly employed, and the glycerin derived from the autoclave process are also used. This plant is especially interesting for the progress that has been made in the last four years in the perfection of the heat economies in distillation. The process employed is the patented one of F. J. Wood<sup>1</sup> which refines a previously purified glycerin by a distillation with multiple effect producing pure glycerin for dynamite manufacture and pharmaceutical purposes. A similar plant is in operation in Montreal belonging to Marx and Rawolle, Ltd., of Canada. The process has also been tested out in Europe in a large plant. The purpose of the process which distills the glycerine under the combined influence of steam and vacuum is the economy of heat. The saving of coal is remarkable and is due to the fact that only a single current of steam is employed in the distillation which, however, traverses a series of stills, 1 to 6 in Fig. 3. For this purpose the glycerin is pumped into the stills by centrifugal pumps after it has passed through the heater which gets its heat from the steam boiler. It flows into the stills in the form of a fine spray in a direction opposed to the steam current which comes from the distilled water evaporator. By the combined action of the vacuum the glycerin is vaporized and rises out of the still into the hot water condensers, 1-6. The temperature of these condensers is adjusted by automatic pressure regulators so that the glycerin is condensed while the steam passes on uncondensed into the next still where it meets a further spray of glycerin as in the former case and with it passes to the condenser tube and so on through the series. Each time the glycerin is condensed it gives up its latent heat to the boiling water employed in liquefying the glycerin vapors. In the wide outlet tube shown on the right the water vapors pass separated from the glycerin into the next still. A similar vacuum is maintained throughout the whole system in order that the steam may not pass, as it did in the earlier apparatus, down through the glycerin, but rather that the glycerin courses down through the steam. In this way a back pressure against the steam current is avoided and the water and glycerin vapors can pass unhindered through the whole system. After the steam has passed through the whole condensing system it finally arrives in the cold water condenser. The further employment of all waste vapors and effluents is also remarkable. The vapors arriving in the boiling water condenser above the fluid are carried to a main above these and from there go downward partly to the distilled water evaporator from which the stills are fed and partly to the sweet water evaporator where it comes in contact with the current of steam coming from the second sweet water evaporator. The sweet water evaporators get their charge from the condensed water which still contains a small quantity of glycerin. This

<sup>1</sup> U. S. Pat. 91,044; German Pat. 217,689; *Chem. Ztg. Report* (1910), 45. See also Wood and Langmuir, *Trans. Am. Inst. Chem. Eng. and Chem. Ztg.* (1910), 99, as well as Ubbelohde-Goldschmidt's "Handbuch der Chemie und Technologie der Oele und Fette," 1911, Vol. 3, Part 2. "Chemie, Analyse und Technologie der Fettsäuren, des Glycerins u. s. w.," p. 100.

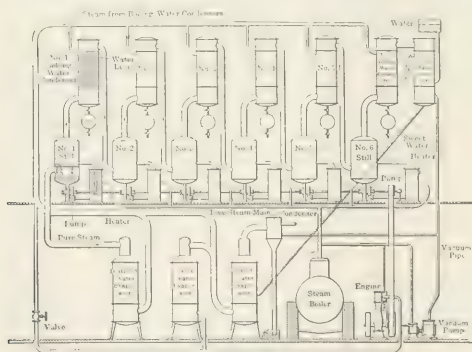


FIG. 3

comes from the cold water cooler at the end of the battery.

This company also operates a shellac bleaching plant. The shellac is first dissolved in a soda solution and then bleached with sodium hypochlorite.

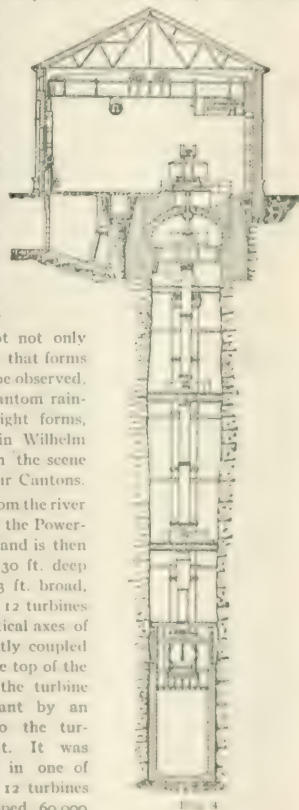
#### IV. THE POWER PLANTS AND THE INTERMEDIATE SILICON-GRAPHITE CO. AT NIAGARA FALLS

These installations lie above the Falls, on the American side. The broad river is divided by Goat Island into two waterfalls coursing between the projecting rock masses, the American Falls 1000 ft. broad and the wildly foaming Canadian Falls! about three times as broad and much more picturesque.

The opinion is rather widespread that the use of the water for the power plants and the various chemical plants has marred the beauty of the Falls. This is certainly not yet the case, for according to the printed description of the Power-house, the mass of water abstracted corresponds to but 4 per cent of the total, corresponding, as our guide informed us, to a lowering stream level by but  $\frac{1}{2}$  of an inch. The only question which remains is whether the scenic beauty of the Falls is diminished by the presence of the various plants. Here we may observe that

the works lie so far above the Falls and viewed from the neighborhood of the Falls appears so small that there can be little objection on this score to their presence. To be thoroughly acquainted with the beauty of the Falls it is necessary to devote to it at least two days of good weather and if possible an evening in full moonlight; this we were fortunately able to do. Then, not only can the double rainbow that forms in the mist of the falls be observed, but also the grayish phantom rainbow which the moonlight forms, such as is mentioned in Wilhelm Tell, Act. 2, Scene 2, in the scene on the Lake of the Four Cantons.

The water is drawn from the river and led by a channel to the Power-house as shown in Fig. 4 and is then let down into a shaft 130 ft. deep through a pipe about 3 ft. broad, at the bottom of which 12 turbines are installed. The vertical axes of these turbines are directly coupled with 12 dynamos at the top of the shaft. We went from the turbine room of one power plant by an underground passage to the turbines of another plant. It was quite remarkable that in one of these works where the 12 turbines and 12 dynamos developed 60,000 horse-power, only 4 gallons of oil were consumed daily, a proof of the excellent annular lubrication of the dynamos, the turbines being lubricated by the water alone, hence Acheson Graphite (Oil-dag) is not here employed for economy in lubrication. The water from the turbine drops into a still deeper shaft and is conducted by a canal to the river below the Falls. Among the



power plants and factories above the Falls are the Acetylene Works, the Castner Electrolytic Alkali Works, the Niagara Lead Works, the works of the National Food Co., of the Carborundum Company and of the International Acheson Graphite Co. I visited only the last of these plants where, however, I also had a chance to see carborundum made as a by-product, and I also inspected one of the American power plants.

In the International Graphite Works, Dr. Acheson himself guided us. He took us into his office and showed us the graphite which he has introduced for some years as a substitute for oil lubricants in steam cylinders, etc. It is almost chemically pure carbon. The history of the manufacture of this graphite is a development of Acheson's work<sup>1</sup> on carborundum. Hoping to get an abrasive which would be harder than the diamond, he melted a mixture of clay and coal dust in the electric oven. Instead of getting a diamond like form of carbon, however, he got hard blue-black crystals of silicon carbide which is known as carborundum and used as a diamond cutting material. Later the clay was substituted by sand and the coal by coke. It was soon shown that on the elevation of temperature, the silicon carbide produced according to the reaction  $\text{SiO}_2 + 3\text{C} = \text{SiC} + 2\text{CO}$  suffers a decomposition into silicon and graphitic carbon. Therefore in the preparation of the Acheson graphite it is not a question of the direct conversion of coal into graphite but its manufacture through the intermediate product silicon carbide. While the presence of mineral substances in the coal employed originally was not necessary, still these mineral impurities are advantageous to a good yield of graphite. The furnaces in which the graphite is formed are about 30 ft. in length and about 3 sq. ft. in cross-section and are covered both on the bottoms and the sides with carborundum plates. The side walls which are installed without the use of any binding material are taken apart after each firing for the removal of the charge. The electrodes consisting of coal and of copper are built in at the ends of the furnace and are then connected with the source of the current, which is alternating. The charge (anthracite or coke mixed with sand) is simply covered with coal dust or fine clay and through this layer the silicon vapors pass producing beautiful crystalline aggregates of carborundum, some fine samples of which I obtained. In order to adapt this graphite for suspension in a finely disseminated condition in oil or water, the material is incorporated with an aqueous emulsion of tannin and a very small quantity of ammonia. This process is not possible with the ordinary kinds of graphite. The material is thus rendered applicable for purposes of lubrication. This very fine suspension of the graphite is destroyed by the smallest quantity of hydrochloric acid. It comes into trade in the form of a paste rubbed up with either water or oil and known, respectively, as aquadag or oil-dag. The latter is made from the aquadag by grinding with oil until the water is completely expelled. In the United States natural graphite has been produced for some time. Between 1900 and 1907 the yield remained fairly constant and fluctuated between 2000 and 3000 tons. It is obtained chiefly in North Carolina in the central and western portion of the state. In the year 1907 the production of Acheson graphite amounted to 4000, a noteworthy increase over the 450 tons which had been made seven years before in 1900. This graphite constitutes a very favorable quantity<sup>2</sup> as compared to the quantity at that time (1907) imported which amounted to 23,000 tons.

#### 1. ACHESON'S WORK ON CARBON

Of the literature on this work which, I cannot say my present I shall make but brief mention of the following, since their more complete discussion will necessarily follow by other authors:

1. The International Association for the Study of the Properties of Carbon, 1911, 1912, 1913, 1914, 1915, 1916, 1917, 1918, 1919, 1920, 1921, 1922, 1923, 1924, 1925, 1926, 1927, 1928, 1929, 1930, 1931, 1932, 1933, 1934, 1935, 1936, 1937, 1938, 1939, 1940, 1941, 1942, 1943, 1944, 1945, 1946, 1947, 1948, 1949, 1950, 1951, 1952, 1953, 1954, 1955, 1956, 1957, 1958, 1959, 1960, 1961, 1962, 1963, 1964, 1965, 1966, 1967, 1968, 1969, 1970, 1971, 1972, 1973, 1974, 1975, 1976, 1977, 1978, 1979, 1980, 1981, 1982, 1983, 1984, 1985, 1986, 1987, 1988, 1989, 1990, 1991, 1992, 1993, 1994, 1995, 1996, 1997, 1998, 1999, 2000, 2001, 2002, 2003, 2004, 2005, 2006, 2007, 2008, 2009, 2010, 2011, 2012, 2013, 2014, 2015, 2016, 2017, 2018, 2019, 2020, 2021, 2022, 2023, 2024, 2025, 2026, 2027, 2028, 2029, 2030, 2031, 2032, 2033, 2034, 2035, 2036, 2037, 2038, 2039, 2040, 2041, 2042, 2043, 2044, 2045, 2046, 2047, 2048, 2049, 2050, 2051, 2052, 2053, 2054, 2055, 2056, 2057, 2058, 2059, 2060, 2061, 2062, 2063, 2064, 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One of these visits was to the famous factory of Parke, Davis & Co., in Detroit, where we spent about 2 hours visiting the various shops of the plant, inspecting the manufacture of pills, tablets, the making of extracts and the fine physiological laboratory. Alkaloids are not made in the works but are brought from Germany. As above mentioned, Adrenalin, the active material of the suprarenal gland of the cow, is prepared here by Dr. Takamine's process. The factory furnishes employment for 200 chemists and 7000 workmen and is very likely superior to any of the pharmaceutical divisions of the well known German chemical works.

In the world-famous stock-yards of Swift & Co. and Armour & Co. we saw the slaughtering of pigs and cows which are butchered daily by the thousands. Here with the most astonishing rapidity, they are killed, skinned and dismembered into all the edible or technically useful parts. Everything is done in the most cleanly manner. The preparation which is perhaps of most interest to the chemist is the manufacture of margarin which is an important process in America. It takes place in apparatus, however, which is of the simplest structure and involves no novelty. A mixture of milk, cream, oleomargarin, lard, cotton seed oil and salt are churned in a machine of known construction<sup>1</sup> and the product is treated with ice and filtered water according to processes which give it the peculiar butter-like consistency. The mixture is then placed in a kneading machine also of known construction<sup>2</sup> where the excess water and the buttermilk are pressed out and finally salt is mixed in. Then follows the shaping, pressing, cooling and packing of the butter.

In the Illinois Steel Works in South Chicago we witnessed the preparation of cast iron from the ore in the many blast furnaces of the plant. We then saw its conversion by the Bessemer process and the rolling of the great Bessemer billets into rails and plates. As I am not specially acquainted with the industry and spent but two hours in visiting these monstrous works, I am not able to judge of any important novelty employed in the practice, which is not already shown in our Rhine factories. The gigantic character of the operations and the speed employed especially in the Bessemer converter plants and in the rolling mills, aroused our most intense interest. It would indeed take a more skillful pen to describe adequately the immense iron industry of the United States and the works such as are at Pittsburgh and Chicago.

I may further mention that we visited the Ford Automobile works in Detroit. Here there is an annual production of 75,000 cars and works corresponding in their dimensions to this immense production are found here. It need not be said that even the chemist is specially interested in very ingenious construction of the machines used. These work with extreme speed and with the greatest accuracy produce the many thousands of single parts employed in the manufacture of the cars. Since these machines stand rather close together and the threatening cranes passed us every moment, we had to pay especial attention to our safety. The measures taken to minimize the risk of accident are not as numerous as with us in Germany and we had to adopt the American motto "Help yourself" as the best danger signal to keep us from harm. This counsel we found necessary wherever we went. The actual consumption of oil for lubrication and tempering is not very large considering the immense amount of oil used in the works. Most of the machines are so devised that the oil used in their lubrication is caught as it drips from them and is pumped back again to the bearings. I have been informed that this plant has a yearly output of cars corresponding to the total German production for the year, *i. e.*, 100,000. It may be mentioned in contrast that while the American automobile is produced at a considerably cheaper price than the

German machine, the taxicabs in New York and other American cities demand an astonishingly high rate of fare. As far as the character of the American automobile product is concerned I cannot speak with authority but the fact that they do not take part to any large extent in the International races, is possibly the reason why they are regarded with disfavor by German experts.

In the many rapid and long trips, however, which I took in American automobiles, both in the works of the Vacuum Oil Co. in Schuylar and in the visitation of the American factories and the extensive tours throughout the country, I have never been stalled or delayed on the way. Moreover, in the American works the chemist or director of the factory frequently has a car of his own and has no difficulty in driving it himself. It happened that our journey took us to Chicago just as the members of the Congress taking the two official trips, arrived there. We met in the Hotel La Salle. In Chicago these two trips divided, the long trip going westward through Denver and Salt Lake City toward California, those taking the short trip going to Cleveland, then to Boston and finally to New York. The renewal of our acquaintance with these members of the Congress was most cordial. In the short time that we were together we exchanged experiences and impressions of the tours that we had thus taken and the direction and management of both these trips was praised in no small degree by all. Dr. Day again tried to induce me to accompany the party to California but my engagements prevented me from doing so. Before our farewell we all met together at the Sherman Hotel which was the headquarters of both trips in Chicago and had a very fine luncheon and then together we saw the slaughter-houses which I mentioned above. Again I had a chance to see Niagara Falls and met there, on the return journey, the members of the Coal Tar trip, 22 in number. We foregathered at a pleasant sociable *kommers* where a German colleague, Dr. Ornstein, as a representative of the German Club, received us. Next day we parted from our company since I had to go with my two companions to Toronto by steamer and then down the St. Lawrence River into Canada, after passing through the famous Thousand Islands. The latter portion of this trip, however, was spoiled by rain and cloudy weather so that the trip through the Rapids could not be taken and we were forced to proceed by rail to Montreal which we found most beautifully situated. Here we were recompensed by fine weather and by attractive places of interest. We were most impressed by the fine twelve story railroad station of the Canadian Pacific, the Dominion Square and the well laid out university with its sporting fields upon which the students played in their odd uniforms. Throughout the U. S. not only have the universities their sporting fields but we found the employees of the Bureau of Standards provided with tennis courts as well.

#### CONCLUSION

Our journey back to New York was made by way of the White Mountains which lie near the Canadian border. Their impression upon us was spoiled by rainy weather. The lack of sign posts hereabout, an index of the American "Help yourself" policy, led us into a rather dangerous situation. We visited a gorge which Baedeker unwarrantably recommended and on our way back from this would-be gorge to make our train connection we had to walk between or beside the railroad rails and part of the way led over a long open trestle, provided with no hand rail and which crossed a deep abyss. We finally escaped this danger and arrived in New York on Oct. 1st after a stop in Boston which, I regret, was only for a few hours. I visited then those works above described which are located in the vicinity, discharged some remaining personal obligations and made ready for my return trip.

On the 8th of October, two fellow tourists and myself boarded the "Nordam" of the Holland-American Line, all of us inspired

<sup>1</sup> For further description of construction see Hefter, *Technologie der Fette und Öle*, Vol. 3, Pp. 114 and 115.

<sup>2</sup> *Ibid.*, p. 146.



with the hope of revisiting shortly this intensely interesting and hospitable country. We were this time the only chemists aboard the steamer, which carried only 29 first-class passengers and we were well looked after. Well satisfied with the trip during which good weather prevailed, we reached Rotterdam on the 18th of October. After three days of a leisurely sojourn in this unfamiliar ancient art center of Holland, I completed my journey by a visit to the Germania Oil Works at Emmerich on the Rhine. This is the first German plant for the hydrogenation of oils, and it daily converts dozens of tons of oil into hard white fat by catalytic hydrogenation.

# TRAVELS THROUGH THE UNITED STATES IN CONJUNCTION WITH THE EIGHTH INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY AT NEW YORK, BY MEMBERS OF THE CONGRESS<sup>1</sup>

By R. HOLDE, *University of Chemistry*

The following account of a tour through the United States carried out, in conjunction with the Eighth International Congress of Applied Chemistry at New York, by a number of the members of the Congress (a tour which was arranged by the Congress and known to the participants as the so-called "Long Trip") will serve to supplement the excellent account of Prof. D. Holde, Zehlendorf-Berlin, entitled "Impressions of the Eighth International Congress of Applied Chemistry at New York and of Various Branches of Industry in the United States,"<sup>2</sup> as well as the abstract of Prof. Freund,<sup>3</sup> Frankfurt, on the so-called "Short Trip," with a short résumé of the details of the long trip. Circular No. 3—"Announcement, No. 3, General Information, Program of Excursions and Factory Visits"—contained an outline of eleven tours, of which one, the visit to Yellowstone Park, was to take place before the Congress, while the other ten were to be devoted to the study of the various branches of industry in the United States. An excellently prepared map, attached to the pamphlet, showed the various localities to be visited and the route while a classified list of the works showed which firms had opened their factories to the Congress. Another such opportunity for becoming acquainted, in so pleasant and comfortable a manner, with American industry, and of obtaining a comprehensive view of its position and condition, would not so readily present itself again to the German. These considerations led me to subscribe as a member of the longest tour planned; this was to comprise a trip through the East, down to the South, over to the West and then back again to the East by way of Canada. Announcement No. 4, however, brought a radical change in the original plans for the excursions as the subscriptions thereto had not arrived in sufficient quantity. Hence, only two excursions were planned, the "Short Trip" and the "Long Trip." The former was to consist of a ten-day tour, taking in Philadelphia, Pittsburgh, Niagara Falls, Detroit, Chicago and Boston; the latter, lasting thirty-six days, was to include in common with the "Short Trip," all the cities up to Chicago and then proceed through Denver, Salt Lake City and Bakersfield to San Francisco; then, after a tour of the States of California, Arizona, New Mexico and Texas, reach the southernmost point of the route—New Orleans—and return to New York by way of Alabama, Tennessee, South and North Carolina. I subscribed as a member of the "Long Trip" and on the 22nd of August, eagerly left Hamburg on the "Cleveland," to embrace this opportunity for a glimpse of the interesting industries of the land of unlimited opportunities.

In spite of the discomfort suffered by many on account of the stormy weather we encountered, the trip across the ocean was

most pleasant and interesting; in the company of both younger and older colleagues, the days flew by only too quickly. After a short stay at the Hotel New York, we started on our journey. As we set foot upon the shores of America, it was with the pleasurable certainty that we should see much of interest and much that was new in this country so rich in industry and that we should get in intimate touch with our American colleagues and co-workers—thanks to chemical literature, we already knew them by name—thereby obtaining new stimulation for our own work.

The exceedingly interesting account of my Colleague Prof. Holde contains everything of importance about the general procedure of the Congress, so that I need devote but little space to this phase of my visit to America.

Even though, as so often happens at so many Congresses, the part devoted to entertainment did not usurp so much of our attention that we lost sight of the main object, attendance at the various discussions, still there were, in New York, other causes to which Prof. Holde has already called attention, which had a tendency to lessen attendance at the meetings. Of these, a number of insufficiencies which were noticeable in the organization of the Congress, and the exceedingly hot and sultry weather, to which we Germans were not accustomed, were the most important. Valuable time was needlessly consumed in waiting for admission cards to the various activities, etc. The deficiencies in the organization of the Congress became the more prominent because the general well-being of the German members was very much upset by the close, muggy climate of New York, together with the very cold drinks and the highly seasoned food which are not always acceptable to the German stomach. A great many of the members of the Congress were compelled to remain in their rooms for shorter or longer periods in order to afford outraged nature an opportunity for rest and recuperation.

The consequences of this general indisposition were, moreover, felt in still other ways. The number of those who were to participate in the "Long Trip," instead of increasing, actually decreased. Many of those who originally had expressed a desire to make this excursion, hesitated to go as they feared the difficulties of the journey, which were much overestimated because of the experiences during the Congress. Immediately after the Congress many had to seek out more congenial localities and climates where they could recover from the strain of the days at the Congress. At times it appeared very doubtful if the "Long Trip" would take place at all. In the course of the common tour of the "Long" and the "Short Trips," however, the number of tourists for the "Long Trip" was once more increased, the new recruits coming from the ranks of the members of the "Short Trip," as many were imbued with renewed courage as a result of the wonderful and happy course of the common journey. About sixty-five, mostly Germans, comprised the personnel of the "Long Trip."

The "Long Trip" was in charge of Dr. David T. Day, head of the Petroleum Division of the Geological Survey at Washington, and of Dr. George D. Rosengarten of Philadelphia. Aided by the local committees in various parts of the country, these two gentlemen had organized and prepared the trip so excellently that it met with splendid success. The members of this excellent and highly interesting tour will always remember them with the greatest pleasure and the sincerest gratefulness. Under the faithful leadership of these two gentlemen, aided by the members of our profession and the various local committees, the journey through the states gave us a clear and concise view of all that the American's country offers and of all that which he, after hardy battle, has wrung from nature. The greatest contrasts were offered those participating in this excursion. For example, after we, with the complacency which comes from a knowledge of a well used steam engine,

<sup>1</sup> Translation made by The Chemical Club Library from *Chemiker-Zeitung*, 37 (1913), 899, 860, 903, 946, 1045, 1104, 1138, 1144, 1270, 1311.

<sup>2</sup> *Chem. Ztg.*, 37 (1913), 2, 53, 86, 129, 158.

<sup>3</sup> *Ibid.*, 37 (1913), 101.

provided with food and drink, looked out from our observation car upon the Mojave desert and learned to know it with all its desolation and barren soil, there was presented to us a picture of that paradise—California—which the American has created out of a desert wilderness by means of irrigation.

The reception everywhere accorded the excursionists showed Americans from an angle whose praises should always be sung. We learned to know the great hospitality of the American, who is only too glad to afford a few hours of pleasant rest and recreation to a weary, wandering stranger. Many an hour, to which we look back and always shall look back with mingled feelings of pleasure and the greatest gratefulness, was spent in hospitable American circles. Finally, the inspection of numerous processes in the most varied branches of applied chemistry and its allied sciences gave us a most interesting and accurate idea of what the American has accomplished and does in this branch of industry. For the most part, the visits were well-planned and executed. Usually, an auto, omnibus or carriage was waiting to take us quickly to the factory which we were to inspect. In general, we were received most warmly and, as a rule, but little was withheld that might be shown. Yet, the various visits were very different both in kind and in results. In the beginning when the "Long" and the "Short Trips" were together, many of the visits suffered because of the large number of participants, particularly the large number of women recruited from the ranks of the local chemical and trade circles. It often happened that the ladies and the professional people who were but slightly acquainted with the process, its control and operation, would remain standing at relatively unimportant points which, though they appeal very strongly to the layman, have but little significance for the scientist. On this account, inspection tours suffered frequent interruptions, progressed but slowly and the time devoted to the more important aspects of the problem was so curtailed that in many instances the manufacturer could not arrive at a question of costs. In many of the tours, particularly those in the West and in the South, the lack of organization was greatly felt. When, however, it was simply a question of showing about but few people, the American was seen at his best and but little was withheld from inspection. The lack of organization in the tour became noticeable as soon as larger groups had to be accommodated. Instead of facilitating matters by dividing the excursionists into small groups, an attempt was made to hold the large company together. These efforts did not always meet with success for while the manufacturer tried to push forward to the discussion of points which, to him, were of the greatest interest and importance, the group would often, as I have before noted, stop at the *unessentials*. In those instances where Germans, or those familiar with German methods, had charge of a tour, the inspection went along easily and without a hitch. We Germans are more accustomed to showing through our plants large groups of visitors, more or less remotely interested in the process of manufacture, than Americans, particularly those who control the factories of the West and the South. The organization of German tours was best seen at the atmospheric nitrogen recovery plant at Nitrolec, South Carolina, where, after the splendid introductory remarks of Mr. Pauling, the comparatively large number of excursionists was divided into three groups and shown through this most interesting establishment under the guidance of the three German engineers connected with the plant. Profiting by the above-mentioned experience gained in regard to American guidance, the members of the excursion were led to adopt an organization which proved a very happy choice but which, unfortunately, was done only in the latter half of our trip. In order to learn the most possible about the various works in the relatively short time at our disposal, there were put under the direction of our chief guide representatives of the respective industry among the excursionists

and by means of explanatory talks, both during the inspection of the plants and after we had resumed our journeys, they informed us of the various details of a given process or factory.

With feelings of sincerest gratefulness and utmost appreciation we shall always remember our two leaders, Dr. Day and Dr. Rosengarten, who gave us such valuable aid in so many different ways. Both gentlemen, having a perfect command of the German language, not only made their explanatory remarks in German but also acted as interpreters between Germans and non-German speaking Americans so that any information tendered by the latter was put at the disposal of those members of the trip to whom the language of the country was more or less of an unknown quantity. Unfortunately, Dr. Rosengarten was compelled to withdraw from the excursion at San Francisco as he became seriously ill with typhoid. Thereupon, Dr. Day devoted himself to our needs with re-doubled zeal and he left us only at Washington after we had boarded the train for New York. To both these gentlemen do I, on this account—I am quite sure all my companions are in perfect accord with me—once more extend the sincerest thanks of all those participating in the excursion, for the splendid way in which they organized and conducted this trip and for the assistance and the many personal courtesies shown us.

The program of these excursions—the "Long" and the "Short Trips"—which were under the direction of the Pennsylvania Railroad, was set forth in an excellently prepared pamphlet (containing a goodly number of illustrations and a fine map) entitled "Tours of the Members of the Eighth International Congress of Applied Chemistry, 1912." The special train which the Pennsylvania Railroad placed at the disposal of the so-called "Long Trip"—the Pacific Tour—consisted, besides the powerful locomotives put on by the various railroads on the different stretches, of a baggage-car, a smoking car, a dining car, two twelve-section sleepers with drawing rooms, two sixteen-section sleepers, a car with ten state-rooms and an observation car with six state-rooms. This very large (considering the comparatively small number of participants) and, therefore, very comfortable train received us on the forenoon of the 16th of September, 1912, and for the thirty-five days which were to comprise the trip, served us, almost exclusively, as our home. Because of its splendid equipment, we were always glad, after we had completed any given tour, to return to the comparative rest and quiet of our peregrinating home. Only in three instances—in Chicago, in San Francisco and in Los Angeles—did we resort to the use of a hotel. Limitations of space prevent me from dilating on the equipment of our train but I may, however, call attention to the fact that, for the great distances which come into consideration when it is a question of getting from one large city in the United States to another—distances which have absolutely no counterpart in our German problem—the equipment of railroads is well taken care of. If there were the assurance of the same degree of safety as that enjoyed in Germany, railroad travel in the United States would be an exceedingly pleasant affair. During our thirty-five day tour, we ourselves underwent much that serves to remind us of the great danger attendant upon American railroads. For this reason when, at the close of our trip, the train was once more bringing us back to New York, it was with a certain feeling of joy and satisfaction that many of us greeted the rapidly approaching city. This joy and satisfaction originated in the fact that neither he nor any one of his traveling companions had suffered any injury or harm during a railroad journey fraught with so many dangers.

The following statistics will give an idea of the danger of American railroad travel: In the period from July 1, 1911 to July 30, 1912,<sup>1</sup> there were 8215 derailments on American railroads; 10585 persons were killed and 169,538 injured; both of

<sup>1</sup> *Zeitschr. Vereins deutscher Eisenbahnen*, issue of Feb. 5, 1913.



these figures are much higher than the corresponding ones for the preceding year. For the operation of the Prusso-Hessian Railroads the corresponding figures for 1910-1911 are: 243 derailments, 645 killed and 1554 injured. While the total number of passengers carried on the Prusso-Hessian Railroads during the year reached the grand total of 1038 million people, the corresponding number for the United States during 1912 was only 971 million. According to the investigations of the United Railways Bureau, the derailments in America are mainly due to the poor condition of road-bed and rails.

That this is actually true, we had an opportunity of ascertaining for ourselves at a derailment of our special train on the Santa Fé, on the stretch between Seligman and Williams, Arizona. Fortunately there was no injury to either the travelers or the train crew. Under the weight of the train, the ties sank into the very poor road-bed; the rails, being inadequately fastened to the ties, became loosened and actually swung in the air, thereby causing a partial overturning of tender, baggage and dining cars. At one point, the massive rails had been broken off clean, showing a hole in the lower part of the rail-head, which surely indicated that in so far as its value and utility was concerned, this rail left much to be desired. A number of the excursionists took some sample pieces as souvenirs from the scene of the accident and these bear mute testimony to the fact that not as much care in the choice of rails is shown in the U. S. as in Germany. In addition to a number of minor railroad, auto and carriage accidents, which altogether passed by without affecting the general well-being of the travelers, we experienced a collision between an electric railway car and a freight train in Los Angeles, Cal. Fortunately, however, because of the diminished speed due to a grade-crossing, only one car was rendered unserviceable, while, aside from a few minor injuries and the shock, we excursionists came out of the collision unharmed. I, as well as the other participants in this tour, am firmly convinced of, and delighted with, the comfort of American railroads, comfort which becomes absolutely indispensable on the long distances one must travel *via* railroad—distances, which in every case are much greater than anything we have in Germany. But nevertheless, because of the relatively greater safety, we shall always find travel on our German railroads much pleasanter. In the course of thirty-five days we covered a distance of about nine thousand miles, visited 25 cities and traveled through 22 states of the United States.

#### PHILADELPHIA

At nine o'clock, on the morning of Monday, September 16, 1912 we started from the Pennsylvania Station, New York, with Philadelphia as our first goal. In the historic chambers of Independence Hall, those venerable chambers in which the American Declaration of Independence first came into being, we, together with the members of the "Short Trip," received a most enthusiastic reception, being welcomed by the mayor of the city, Mr. Rudolph Blankenburg, a native-born German. For the various tours through the city and its magnificent parks, of which one, beautiful Fairmount Park, is the largest in the United States and has an area of about 3500 acres, as well as for the inspection of a number of its factories, we broke up into various groups. The visit to the Philadelphia Mint showed that the various machinery used in American mints is the same as that used in Germany as well as that which I have seen also in Vienna and London. We were not shown the separating room for the various substances containing the noble metals, but the process employed is the same electrolytic method used in so many other plants. Prof. Holde has given an excellent account of the Petroleum Refinery of the Atlantic Refining Co. which I next visited, so I need hardly go further into that.

#### PITTSBURGH DISTRICT

That same night, we left Philadelphia, reaching Pittsburgh

on Tuesday morning; we remained there until Wednesday evening. In a most voluminous handbook with which the excursionists were provided, a comprehensive survey of all that could be visited was given not only by means of a list of the plants open to inspection but also by articles on Pittsburgh and its various phases of industry.

The main excursions—in which I also took part—were devoted to an inspection of the Clairton Steel Works and Blast Furnaces of the Carnegie Steel Co. at Clairton on the Monongahela River, a visit to the laboratories and experimental stations of the Bureau of Mines and the Bureau of Standards and an inspection of the Water Filtering plant of the city of Pittsburgh. From the first of these a most interesting return trip was made down the Monongahela through that fascinating industrial district on a river-steamboat (which, considering the smoke-befogged and sooty locality, bore the highly euphonious but inappropriate name of "Sunshine"). On the last afternoon I visited the Pennsylvania Smelting and Refining Works, at Rosslyn Station, Carnegie, Pennsylvania, in the company of Dr. Heberlein of Frankfort and his assistant Mr. Bickle. I also made a short trip through the Carnegie Institute of Technology and the Carnegie Library.

The city of Pittsburgh is situated in the state of Pennsylvania, at the junction of the Monongahela and Allegheny Rivers, which unite here to form the Ohio River. A most important shipping center has grown up at this point which forms the natural gateway between the East and the West and lies in the midst of a district rich in natural resources, leading readily to the development of the city as an industrial center. Since the coal, the petroleum and the natural gas essential for the conversion of the rich, available iron ore, occur most plentifully, a tremendous iron industry has been developed in and around Pittsburgh. The coal of this district is bituminous, uniform in quality. Pennsylvania yields about ten million tons of this bituminous coal. About 100,000 Coke-Ovens, of which about 85% are the Bee Hive type, convert this coal into coke. The use of ovens with arrangement for the recovery of by-products is increasing only gradually. Pennsylvania produces about 26 million tons of coke annually in these coke ovens. It also yields about 8-9 million barrels of petroleum (1 barrel = 39.7 gals. petroleum) of a value of about \$1.75 per barrel. The petroleum is rich in gasoline and illuminating oil. Petroleum wells are generally at a depth of 1000-2200 ft. Pennsylvania natural gas consists of 88% methane and 12% ethane. The production of natural gas has an annual value of about 21 million dollars; 1 cubic meter of the gas is now sold for household purposes at a cost of about 32 cents per 1000 cu. ft. while in the 80's the price was only 5-10 cents per 1000 cu. ft. The production of iron ore is decreasing in Pennsylvania and this raw material is, of course, brought in from other localities, particularly from Minnesota, Wisconsin and Michigan.

The Pittsburgh district converts about 14 million tons of iron ore and produces about 7,600,000 tons of cast iron and 6,900,000 tons of steel annually. As a natural consequence there has been developed in and around Pittsburgh an enormous industry which further converts these large quantities of steel and iron. Various other industries, such as the glass and various branches of applied chemistry, also flourish in this locality.

THE CLAIRTON STEEL WORKS OF THE CARNEGIE STEEL WORKS comprise: *First* a blast-furnace plant with three 400 ton blast furnaces equipped with all modern conveniences, together with the necessary compressors, and having a maximum annual capacity of 460,000 tons of iron. *Second*, a reverberatory furnace plant with twelve 60 ton furnaces, a 200 ton mixer, with all accessories; the combustible used for heating these reverberatory furnaces is natural gas; the maximum annual production of Martin steel is 531,500 tons. *Third*, a rolling mill with six rolls, one of which is for plates, etc., with a maximum annual production of 475,000



tons, a sheet mill with a maximum annual capacity of 400,000 tons and four rolling-mills, etc., with an annual capacity of 460,000 tons; in all cases, the furnaces are heated with natural gas. In the various parts of the works about 200 men are employed about the blast furnaces, about 280 men in the reverberatory furnaces and about 700 in the rolling mills, to which figures are added about 600 men in the incidental occupations. The steam boiler plant, consisting of 53 boilers, 40 of which are heated by producer gas, and the remainder with coal, yields about 18,000 horse power and the electrical plant about 2100 kilowatts.

This plant represents one of the ten plants of the Carnegie Steel Co., which, with a complement of 39,000 men in 59 blast furnaces, 13 mixers, 138 Siemens-Martin ovens, 16 converters and the requisite number of rolling mills, produces 7,500,000 tons of iron and 9,000,000 tons of steel annually with a daily consumption of about 40,000 tons of ore, 19,500 tons coke, 10,000 tons limestone, 8000 tons coal and 3,000,000 cubic meters of gas. The blast furnaces of the Clairton Works convert Lake Superior iron ores. The producer gases<sup>1</sup> are not utilized in producer gas machines but serve only as the combustible for the blast heaters and for the steam boilers, while at the Homestead Works at Rankin and at another plant of the same company, the producer gas is utilized to drive nine, and four, respectively, producer gas machines which generate the electricity for the entire plants. The first plant for drying the blast artificially by means of the Gayley process, was installed at the Isabella Furnaces at Etna, Pa., of the Carnegie Steel Co. Three modern blast furnaces of 500 ton capacity, at that place, which serve for the preparation of spiegeles and ferromanganese iron, are equipped with a Gayley air-drying plant with a capacity of 1200 cubic meters of air per minute at a maximum temperature of 32° C. and a maximum moisture content of about 20 grams per cubic meter. The moisture of the blast often sinks below 2.5 grams per cubic meter.

The three hour steamboat ride back to the city was most interesting. In the twenty miles of the run down the river we passed a great many large factories from whose chimneys soot and smoke poured forth so thick and fast that the sun's rays could hardly penetrate through the clouds thus formed. This trip gave an idea of the enormous industry of this locality.

THE SMALL SMELTER OF THE PENNSYLVANIA SMELTING CO. which I visited the next day, has a capacity of 2500 tons ore and 1500 tons lead-plate per month; the maximum capacity of the plant consists of 18,000 tons silver-free lead, 180,000 pounds of silver, 600 tons of crude lead, and 100 tons of litharge for analytical purposes. The plant comprises two water-jacketed furnaces for melting the lead ores, reverberatory furnaces for roasting the blocks, the furnaces and apparatus requisite for refining and de-silverizing the lead-plate by the zinc de-silverization process, the necessary furnaces for the separation of lead and silver, and finally a number of Bee-Hive ovens for the production of the coke for the smelters. The most varied lead and silver ores are converted in this plant, such as ores from the Canadian Cobalt District, lead ores from the Cour d'Alène district in Idaho, etc. The greater part of the ore now being converted is silver ore from the silver, nickel, cobalt and arsenic ores occurring at Cobalt, in Ontario, Canada, ore with a variable silver content. The richest ores contain up to 9% silver, with about 15% nickel and cobalt and 25-35% arsenic; the ordinary ores contain about 3-3.5% silver with 5-6% nickel and cobalt; the ores are essentially silicates. The ordinary ores, after the addition of lime, lead-ore and roasted pigs from a similar operation, are smelted in water-jacketed furnaces, to lead-plate pigs (containing up to 1.8% silver) which are roasted in reverberatory furnaces and go back into the process and are re-worked and to slag. The resulting speiss is melted up once more, in cupolas, with

lead ores having a low silver content, and in this form is said to be sold to German factories. The finest lead-plate coming from blast and alloy-refining furnaces is recovered in English cupelling furnaces, while other grades of lead plate must be refined and go through the zinc-de-silverizing process. The high-grade lead thus obtained then passes through the cupelling furnaces. According to the information advanced, it is preferable to produce the coke from coal in the Bee-Hive ovens by more or less antiquated methods rather than to buy it. It is estimated that this brings about a saving of about 52 cents per ton because coke purchased on the open market costs \$2.72 per ton while when prepared at the plant in the Bee-Hive ovens it costs, with a 60% yield, only \$2.20 per ton.

THE PITTSBURGH WATER-FILTRATION PLANT, situated on the north bank of the Allegheny river, above Aspinwall, is indicative of the effort the various cities of the United States are making to raise the general standard of health of the community by bettering the drinking-water supply. Unfortunately, it is only too true that in most cities of the United States, the use, for drinking purposes, of water which has not previously been boiled, is attendant with grave dangers, for nature seldom places a potable water at our disposal and the resources of the oftentimes splendid filtration plants which have been installed by the larger cities are taxed beyond their capacity by the needs of the rapidly growing communities. Although the Water Filtration plant of the city of Pittsburgh is a most excellent and modern system, the city has developed so quickly and enormously that it relieves but inadequately the demands for the supply of drinking water made upon it. At the several pumping stations along the line, the water is tapped from the Allegheny River and led into settling basins, in which, whenever necessary, it is treated with calcium chloride in order that the acid of any iron sulfate present may be removed, while, at the same time, the precipitated calcium sulfate tends to carry down with it any foreign bodies in suspension in the water. From the settling basins, the water is led on to low sand filters which rest on arches supported by pillars. One part of the Filtration Plant at Aspinwall has been in operation since 1908 but the operation of the other part is yet to be begun. The water passes through the filter diagonally from the top to the bottom and then reaches the reservoir from which it is led to the city through steel pipes. The plant is augmented by a new pumping station. The laboratory of this plant is in the Power House and is equipped with all conveniences and apparatus necessary for the chemical and bacteriological examination of water.

This plant also illustrates the prominent American trait of providing their cities with beautiful parks, to which, after the toil and turmoil of the day's work, one can retire and in the midst of the noise and the bustle of the city find a pretty spot which affords a few breaths of fresh air. It has been so planned that in the course of the natural development of the city, a park will be built about the filters and the reservoirs; the streets of this park have already been laid out, trees, shrubbery, etc., have been planted, and provision made for electric lighting.

BUREAU OF MINES—In 1910, the federal government established the Bureau of Mines which consists of an experimental station for mine building and the same for engineering and chemical investigations. The greatest possible utilization of the natural mineral resources of the United States together with greater safety of miners in their work are the aims of this Bureau. The latter purpose is accomplished by the determination of the causes of mine accidents and the means of lessening their number. Investigations similar to those made in the Mining Institutes of our German High and Trade Schools are undertaken here; explosives are examined and tested in all ways; an experimental gallery is utilized for the study of explosibility of gas mixtures,

<sup>1</sup> Really the Blast Furnace gases.

etc., combustibles are examined, experiments on briquetting, on gas production are undertaken, questions on the abatement of the smoke nuisance and the process of combustion are studied, etc.

The experimental station of the Bureau of Standards consists of a laboratory for the investigation and the testing of construction materials. These are examined chemically, physically and microscopically and their resistance strengths tested by means of loading tests in appropriate apparatus. We were shown the greater part of the apparatus used in both these Bureaus in operation. As a larger experiment on the inflammability of coal-dust, there was carried out, in the experimental gallery, a test of the adaptability of black powder for use in coal-dust mines. A load of 375 grams of black powder was set off in the experimental gallery under conditions similar to those in a coal-dust mine; in connection with this artificial coal-dust explosion, there was a demonstration of safety apparatus for traveling through areas filled with such gases. We were also treated to a practical demonstration of the resistance strength of fire-proof bricks against loads at a higher temperature, and we were shown the operation of electric ovens for the study of the softening of porcelain, etc.

THE CARNEGIE INSTITUTE OF TECHNOLOGY, situated in Pittsburgh and which, though still in course of construction, occupies an area of 32 acres in Shenley Park, is of much interest to members of the technical trades. It was founded by Andrew Carnegie with an endowment of over eleven million dollars, including both buildings and foundation. In four sections, which include both day and night sessions, about 1100 day students and 1300 night students are educated; the men in the various engineering trades; the women who comprise the Fourth Section receive instruction in the various womanly arts such as Domestic Science, Dressmaking, Millinery, Commercial Work and Teaching. In order that those of moderate means may obtain a technical education of approved standards, the cost of tuition is kept at a minimum.

THE CARNEGIE LIBRARY—There is still another institution in Pittsburgh which was founded by Andrew Carnegie and which is also devoted to the education of the masses. This is the Carnegie Library, the largest of its kind founded by Carnegie. In 1895 it was opened with only 9000 volumes on its shelves; now it contains about 400,000 volumes, has 8 branches in various parts of the city which contain mostly more popular works (so that in many cases borrowers are spared the long trip to the Central Library) and 200 small branches all over the city which facilitate the distribution of books. The main library is augmented by a number of special libraries, such as a collection of Books for the Blind and for Teachers of the Blind, a technical Division for Workmen, Engineers and Manufacturers with a collection of Patent Specifications, etc., a collection of trade catalogs, etc. Among other branches of the Technical Division, there is one on Telephony and in addition it contains concise information and bibliographical lists for the investigation of special subjects. I had the opportunity of visiting very many public and secondary school libraries in the United States, such as the John Crerar Library in Chicago, the Public Library in Boston, the library of the University at Palo Alto, Cal. From these visits I may safely conclude that the public libraries of the United States, which are meant to be educational institutions for rich and poor alike, have been wonderfully developed and splendidly organized. Practically every large city boasts a larger or smaller library, built and maintained by either private or public means, in which the reading and educational needs of both rich and poor, young and old, are admirably looked after; there is even a special division for school children—always equipped with a large, well-furnished and well-lighted reading-room in which they may slake the youthful thirst for knowledge. The card catalog system is so well organized that any book

whose author or title is not accurately known can be located without much trouble. The way in which the libraries, with all their splendid equipment of reading-rooms, etc., is placed at the disposal of everyone is worthy of much praise. Fortunately, in all parts of Germany we, also, are becoming conscious of this need (so readily recognized and aided by private capital of the rich American industries in the United States) and of the desirability of placing the large libraries of our secondary schools, with their priceless treasures, at the disposal of the public.

#### NIAGARA FALLS

After a ride through the night had taken us from Pittsburgh to Buffalo and thence to Niagara Falls, we visited, on Thursday morning, the works of the International Acheson Graphite Co. at Niagara Falls, and the Power Houses of the Niagara Falls Power Co., as well as those of the Ontario Power Co. of Niagara Falls and the Ontario Transmission Company, Ltd. The wonderful weather added to the pleasantness of our tour, so that we were able to view the Falls in all their full force and majestic beauty and gaze with rapture and amazement upon the white, foaming masses of water, the downward plunge, and the seething, frothing whirlpool formed below. When in October on a little trip to Canada, I once more visited the Falls, how different was the picture as I gazed upon the waters through the fog and the mist with which all-harmonious nature had enveloped them. Throughout our 35 day tour we were particularly fortunate for we were practically always blessed with just such charming weather as that which greeted us at Niagara. As a result, everywhere we went, we saw the country at its best, and in memory there still remains a picture of the beautiful aspect, the beaming sun, the azure depths of heaven, nature at its best. One day in Chicago, one day in New Orleans and one day in Great Falls, these were practically the only rainy days we encountered during the entire trip. How different, how much less pleasant would have been our tour if we had been forced to cope with inclement weather! Many a visit would not have passed so easily and so smoothly. Many of the industrial plants lie on the outskirts of the city proper, in neighborhoods in which very little is done for the care of the streets and in bad weather the poor and dirty roads are often transformed into impassable morasses. We excursionists will not so readily forget the morass at Great Falls, the trip on the muddy, rain-softened road from Denver to the Globe Smelter. This gave us an idea of just what such neighborhoods can descend to during inclement weather. In contrast to this, as a general rule, the streets within the city proper are well cared for.

THE FALLS—The great Falls of the Niagara, which unite Lake Erie and Lake Ontario, are one of the greatest marvels of the world. By means of Goat Island, the water is divided into two parts, the smaller American Fall, with a drop of about 155 feet and a width of about 1080 feet, and the larger and more beautiful Canadian Fall, the Horseshoe Falls, which is 155 feet high and 2830 feet wide. The quantity of water which is plunged down to this great depth has been estimated at over a half million cubic yards per minute and this could generate an enormous amount of energy of which, up to the present time, only a small quantity has been harnessed and utilized. The energy attainable from the Niagara Falls is estimated at five million horse-power, of which only 367,500 horse-power are now utilized for industrial purposes, about one-half for electrochemical processes and the other half for railways, electric lighting and other industrial purposes.

THE NIAGARA FALLS POWER COMPANY has its power-house on the American side, about a mile above the Falls. The necessary water is led off by means of a canal or conduit and the fall of the same is utilized in two power-houses for the generation



of 105,000 horse-power. Further data on these plants are contained in the account of Prof. Holde.<sup>1</sup>

THE ONTARIO POWER COMPANY, situated on the Canadian side, takes its water about one mile above the ridge of the Horseshoe Falls, and leads it through a subterranean conduit of steel and re-enforced concrete to the Generating Station, situated on a cliff below the falls, where, with the aid of 10 turbines and 10 generators, the electrical energy is obtained, to be then led by means of subterranean cables to the distributing stations above. From the turbines, the water is led back to the river through conduits below the Power House. There are, at present, 10 generators, three of 10,000 horse-power each and seven of 12,000 horse-power each, each of which is coupled directly with its respective turbine by means of a horizontal shaft. The current generated is a three-phase current of 12,000 volts. In the Distribution Station it is transformed to 60,000 volts for the cables which lead it to Queenstown and the wires of the Niagara, Lockport and Ontario Power Co. (which furnishes the current for use in the United States) but to 12,000 volts for the distribution of the current for use in Canada.

Most eagerly did we step from the train after the trip to the Power House of the Niagara Falls Power Co., for, according to the original plans of Announcement No. 3, we looked forward to a hearty welcome at the various plants of Niagara Falls' most flourishing electro-chemical industries. Unfortunately, only part of our expectations was realized. Only the International Acheson Graphite Company opened its doors to us. The Calcium Nitride factory, as well as the Hooker Electrochemical Company (which produces alkali electrolytically by the Townsend process) had withdrawn the permission which they had originally granted for the inspection of their plants. The reasons which led these firms to such action remain unknown to us. The same thing occurred still another time, in the South. Prof. Holde<sup>1</sup> reports at length on the visit to the works of the International Acheson Graphite Company so that I have nothing to add thereto. A round trip on the electric railway down the left bank of the river to Lake Ontario and back again on the right bank to Niagara Falls gave us an opportunity of enjoying the beauties of nature.

#### DETROIT

A ride at night from the 19th to the 20th of September, 1912, brought us to the city of Detroit, a rapidly growing industrial center on the Detroit River, which unites Lake Erie with Lake St. Clair and Lake Huron. The annual traffic through this river is said to be more than double the traffic through the Suez canal; all the freight of the Great Lakes must pass through this river. Detroit is the Automobile City. This industry has been developed here to an enormous extent and its importance for this city was demonstrated to the excursionists by visits to the various automobile factories. I, personally, joined a section which inspected the automobile factory of the Packard Motor Car Company, the Acme White Lead and Color Works and the plant of the Aluminium Castings Co. Together, we then visited the whiskey factory of Hiram Walker & Sons in Walkerville, Canada, and the Chemical Factory of Parke, Davis & Company. A steamboat trip on the Detroit River and Lake St. Clair—during which an aeroplane which was then flying circumnavigated the steamer—closed our most interesting day in the beautiful city of Detroit.

**AUTOMOBILE FACTORIES**—The automobile industry is the chief industry of the city of Detroit. In the course of the last few years, this industry, which, but a decade ago, was but a minor part of the industrial development of the United States, has taken great strides forward. In the year from July 1, 1911–July 1, 1912, the total production of automobiles in the United States was 275,000 cars, of an average value of \$1150–\$1200, of which the Ford automobile factory in Detroit alone produced

75,000, while the total output for the year 1912–1913 is estimated at 400,000 cars. The average value, however, will be lower for this year than for the preceding, because the number of lower-priced cars increases from year to year. The United States exports annually about 30 million dollars worth of automobile and automobile parts. The operation of an automobile factory was watched and studied with the greatest interest by all participating in the excursion. The operation and control of the machinery must necessarily arouse the interest of even the layman. Its construction is often remarkable, and within a few moments can be seen either the formation of an auto part or its coupling to another in anyone of the appropriate machines. If we take into consideration the high prices generally prevailing for most necessities and luxuries, American automobile factories produce comparatively cheap cars. These low prices can be attributed solely to large scale production and to a widespread division of labor. Only a few specific types of cars are built, so that only a relatively small number of machines are required and every individual workman prepares only one, or only a few parts of the final product. This workman, who year in and year out, need go through only a few definite motions can soon perform them in the shortest possible time, so that he produces the part in question in the quickest and cheapest way. But, on the other hand, the advantage of causing a relatively cheap-working industry, brings with it, also, an enormous disadvantage. The workman is no longer a thinking force or hand-worker, but is, instead, only a small part of a big machine. He can easily be replaced by another man, but, he himself, can not readily take up some other industry or independent employment. The more this large-scale production is introduced, the more does the independence of the individual worker tend to disappear. He comes to be directly dependent on his factory so that, if discharged, it is only with difficulty that he can find similar work. We must, unfortunately, admit that in Germany also, a similar division of labor has taken place in many branches of industry.

I, as well as every other member of this tour, together with everyone who has visited smaller or larger plants in the United States, can subscribe to all that Holde, in his account, says of the danger attendant upon visits to the Ford and other factories. On all sides in the various factories and plants, there is noticeable a conservation of space which is not always caused by local conditions and which does not take into consideration the dangers to which the laborers are thereby exposed. I can not guard against the impression gained in the large industrial centers of having seen, much more frequently than in Germany, workmen, who, through accidents, had lost an arm, a leg, etc. We have done much more in the direction of the prevention of accidents so that the number of casualties is much smaller than in the United States, where, in addition to the above conditions, accidents occur very easily because of insufficient protection for moving objects, etc.

**ACME WHITE LEAD AND COLOR WORKS**—Since 1906 the white lead factory of this company has used the Mild Process for the preparation of this pigment. The procedure, in this process, is as follows: The lead, after it has been melted in the proper vats, is brought, by means of hot pipes, from the bottom of the boilers, into the atomizers, in which, through the agency of superheated steam, the molten lead is converted into a very finely divided state. The tiny molten bits of lead fall into steel tanks which are filled with water, thus solidifying and then they are led through worms to the pumps which force them into the settling tanks situated above. After settling, the water runs back to the steel tanks while the lead is brought to the oxidizing apparatus—the so-called oxidizers—in which, after the addition of water, it is mechanically agitated for 24 to 36 hours by means of a blast of air at a comparatively low pressure. The bits of lead which have already acquired a thin layer of suboxid in

<sup>1</sup> *Chem. Zeit.* (1913), p. 158.



the dusting apparatus, react chemically with the air and form basic lead hydroxide with the development of quite some heat, as we ourselves could determine. Eighty per cent of the lead is changed. The material is then put into a trough—the so-called "Float System"—in which the basic oxide and the metallic lead are separated from one another. The latter goes back to the oxidizers, while the basic oxide goes to the carbonators, large wooden vats in which the lead hydroxide is treated for 36 hours with the purified (free, as far as possible from carbon monoxide) chimney gases from the boiler plant. The resulting pure white basic lead carbonate then goes into the drying pans. From this point it receives the customary treatment.

**THE ALUMINIUM CASTINGS CO.**—The aluminium foundry we visited resembled to a great extent all large alloy foundries. The forms and the molds were prepared in the usual manner. The aluminium was melted in smelters provided with a blast from below. The casting temperature is  $725^{\circ}$ – $740^{\circ}$  C. The various parts are soldered together by means of the oxy-acetylene flame. No information was tendered on the composition of either the aluminium and aluminium alloys used for castings or of the solder employed.

**PARKE DAVIS & CO.**—The inspection of the large pharmaceutical factory of Parke, Davis & Co. (whose products can be obtained in Germany) was particularly interesting. Two hundred chemists and 7000 workmen are employed in this enormous plant. We saw all kinds of machines for the manufacture of pills and tablets which were busily turning out their products to satisfy the demands of Americans who seem to have a predilection for pills and treatises. A large, well-equipped laboratory (in which we were, also, given a demonstration of some physiological experiments on animals) proved that science had been accorded a secure position in this plant.

#### CHICAGO

Our special train brought us over night from Detroit to Chicago, our next stop, where we spent three days with the members of the "Short Trip." The separation of the tours was to take place here; while members of the "Short Trip" were to return to New York *via* Cleveland and Boston, we were to continue westward through Denver and Salt Lake City to California. A farewell banquet at the Sherman Hotel on the last night brought us together for the last time for a few pleasant hours. Not only in our own branches of industry, but also in many other ways did those three days in Chicago present us with much of interest. The visit to this city will always be a pleasant reminiscence. As everywhere on our trip, we found everything in Chicago well organized and splendidly executed. The members of the local committee placed themselves at our disposal in the most obliging way and the reception accorded us on all sides was most friendly and hospitable. We visited the various banks, the exchanges, the warehouses of Marshall Field & Co. and the John Crerar Library. The equipment and operation of the banks was most fascinating and we marveled much at the remarkable ability to remember persons shown by the various tellers and officials. The system of cataloging and the equipment for the loan of books, etc., was explained to us at the John Crerar Library, which is a free, public library of scientific and technical literature. A certain German book on Pharmaceutical Preparations which was asked for by its author, one of the members of the excursion, was quickly located in the proper division of the card-catalog and was soon in the author's hands. We also visited and studied the organization and equipment of an American mercantile house.

As far as industrial plants are concerned, I visited the works of Gary Steel Co. in Indiana and the white lead factory of the National Lead Co. A visit to the Union Stock Yards and to the Slaughter-Houses of Swift & Co. and Armour & Co. gave us an idea of one of the important branches of industry of this city, the second largest in the United States. Some of us made

a side trip to LaSalle, Illinois, where we visited the zinc works of the Matthiessen & Hegeler Zinc Company.

Chicago, with its  $2\frac{1}{2}$  millions inhabitants, forms, because of its fortunate traffic conditions, the uniting link between the great agricultural and cattle-raising districts of the West and the industrial plants of the East. An enormous meat industry, without a parallel at any other place on the earth, has been developed at this point. The vast incoming hordes of Western cattle are slaughtered here and every part is made use of. This locality furnishes the meat for practically the entire country. The following figures will give an idea of the enormous operations involved. Swift & Co.—one of the firms engaged in this industry—has a capitalization of 75 million dollars and a reserve fund of over 26 million dollars. About 7000 hogs and 5000 cattle are slaughtered and prepared daily by this firm.

**GARY STEEL CO.**—The steamship ride on Lake Michigan to the iron works of the Gary Steel Co. at Gary was spoiled by mist and rain. As there was no real factory visit, but rather an actual ride on a railroad train here, but a slight insight into this colossal and most interesting plant was obtained. We did not see very much of the place at close range and the opportunity for more intimate inspection was afforded at only a few points. However, the railroad trip gave us an idea of the size of the works. It lasted one and one-half hours and we were allowed to inspect thoroughly the interesting devices for unloading the ore from the ships and for transporting the same to the yards and from there to the blast furnaces. We also saw the Kopper Ovens in operation.

Gary, which lies on the shores of Lake Michigan, southeast from Chicago, in the state of Indiana, is one of the youngest, albeit one of the most important cities of the iron industry in the United States. Founded in 1906, it has witnessed a very rapid development. At the present time it has about 30,000 inhabitants. There are in operation in the iron works 560 Kopper Ovens with accessories for the recovery of by-products, which yield over 200,000 tons of coke a month, 8 blast furnaces with a daily yield of about 400 tons, 23 gas machines, operated by blast furnace gases, 42 Siemens-Martin ovens with an average capacity of 85 tons, a rail and plate rolling mill and a number of rolling mills for other purposes. In connection with this plant there has been a development in Gary of those industries which utilize and convert iron. There are, for example, factories for building cranes, for manufacturing tin, etc. The raw materials for this enormous work come from Lake Superior and are unloaded in the harbor of Gary by means of 10 electrically controlled unloading machines. These can unload as much as 1100 tons of ore per hour. To these are joined ten traveling cranes about 500 feet long which extend from the place where the machines dump their ore, all over the ore yard. Each crane is equipped with a 15-ton bucket for scooping up the ore and bringing it to the reserve piles from which, as required, it is once more scooped up and loaded on the freight cars that bring it to the blast furnaces. The cranes rest on two shafts mounted on wheels by means of which they run up and down the rails laid all over the ore yard. The ore yard has a capacity of 5 million tons of ore. Behind the ore yard are the blast furnaces. Between this yard and the blast furnaces are a large number of raised bins, set in two rows, one for coke and one for ore and limestone. Over the bins are two tracks on which run two electrically driven 60 ton freight cars for the ore. Coke and limestone are brought directly from the railroad over these pockets and loaded into them directly. At the bottom, the pockets are closed by electrically controlled chutes. Alongside these bins are tracks on which run the cars which bring the material to the furnaces. The trip from furnace to bin is made in one minute and on an average each car carries 2.6 tons ore or 2.2 tons limestone or 1.3 tons coke. The car is automatically stopped at the mouth of the furnace. The melting of the ore yields a blast furnace gas

which represents an energy content of 2500,000 H. P. Of this, 30 per cent is used for heating the blast;  $7\frac{1}{2}$  per cent for the production of steam for a special purpose;  $12\frac{1}{2}$  per cent for the blast and 45 per cent for the generation of electrical energy. The blast furnace plant, when in full operation, requires about 4000 tons of coke per day, corresponding to about 5000 tons of coal. The coke ovens are situated on a stretch about 3600 feet long by about 1080 feet wide, and provision has been made for a plant, equal in size, adjoining. The coal is brought to the works by railroad from Pennsylvania and Ohio.

The coal not used directly for various purposes is stored in a yard which has a capacity of 350,000 tons, and in which the same devices are used for loading and unloading as in the case of the ore. The coal required for immediate consumption is put into  $3 \times 4$  bins of about 50 tons capacity, from which by means of shakers it comes to the conveying belts. These carry the coal to the crushers where it is crushed, in 4 coal-breakers of a capacity of 350 tons of coal per hour, to a fineness of 40 mm. and then further ground, in 8 coal-mills with a capacity of 250 tons per hour, to such a degree of fineness that 80-85 per cent will pass through a 32 mesh sieve. From here, conveyors take the coal to the two mixers in the middle of the coke oven plant; these have a total capacity of 1700 tons of coal. From here the coal is brought by means of conveying belts to 4 coal-chutes, each of which holds 2100 tons coal. From these chutes the coal is let down into 4-part, electrically driven cars, which load the coal into the ovens through their four loading holes. The ovens are grouped in two rows about 200 feet apart; each row is divided again, so that the total oven plant consists of 4 groups about 630 feet long, 88 feet wide, each of two batteries of 70 ovens each, so that the total number of ovens is 560. The coke ovens are the well-known Koppers Regenerative ovens. Each chamber is 3700 feet long, 10 feet high and 1.6 feet wide in the middle and can hold  $12\frac{1}{4}$  tons coal. It takes over 16 hours to feed one of these ovens. The yield of coke is about 82 per cent weight of dry coal. The total capacity of an oven is about 13 tons for every twenty-four hours, which is rather high, in fact, much higher than is the case with us. This is because the oven itself is comparatively large and the feeding-time relatively short. Since a very large plant comes into consideration, mechanical power is used to a great extent in the operation of these ovens. Large emptying and rolling appliances take care of their respective work. One oven is loaded and emptied every three minutes. While the glowing coke is being washed by a strong stream of water it falls directly into an extinguishing car, which is then brought, by means of an electric locomotive, to one of the four quenching towers, where the coke is completely quenched by two perforated water tubes. The car is then brought to the coke sieve and emptied into two containers which are above the sieve and empty directly into it. Here it is divided into coke dust, fine coke and blast furnace coke, about 92 per cent of the latter being obtained. The coke oven gases are converted into by-products—tar and ammonium sulfate—by the direct process of H. Koppers, and about 120 tons of tar and 30 tons of ammonia are recovered daily in this way.

THE NATIONAL LEAD CO. makes all kinds of lead products. In the white lead division this substance is made by the "Old Dutch" process. The lead is cast into perforated sheets and is then filled into earthenware pots, in the lower, restricted parts of which there is acetic acid. These pots are placed in moist tan-bark in large rooms and after being filled with the lead, are covered entirely with the tan-bark. In this way a room is filled with rows of superimposed beds. By means of the heat thus evolved, acetic acid vapors are formed and these act upon the lead, converting it into the acetate which is then transformed into a basic lead carbonate by the carbonic acid (formed by the decomposition of the tan-bark) and enters through holes

in the pots. The acetic acid which is re-liberated enters once more into reaction, causing the further formation of lead acetate. This process continues for several weeks until practically all the lead has been converted to white lead, which can be then obtained by clearing the chamber. This white lead, containing a little metallic lead, is then brought into sieves in which three kinds of white lead—the fine, the coarse and that polluted with metallic lead—are separated. The coarse and the fine white lead are ground in a rolling mill and then brought to grinders by means of buckets. The ground material is then either packed directly for use, in kegs, or it is put into a mixer, together with linseed oil, and rubbed up to a pigment. The finished, pastry pigment is packed in small kegs for the market. Mechanical appliances have facilitated all stages of the process. The plant has an annual yield of 1200 tons of white lead. It also produces about 4000 tons of litharge and 5000 tons of various lead alloys each year. The various intermediate compounds—oxidized products, etc.—occurring in the different processes are melted up and reduced to lead.

#### DENVER

At noon on September 24th we unwillingly left Chicago and our worthy hosts after spending  $3\frac{1}{4}$  days in that neighborhood. We realized only too well that the time had been indeed short for gaining an intimate knowledge of Chicago and the industries which make it. For nineteen hours our train proceeded westward to Denver, the beautiful capital of the state of Colorado. Denver is typical of the modern cities of the United States and ranks as one of the most beautiful of them. A tour of the city, which at the same time brought us to the various plants we were interested in, showed us its beauties. On the one hand are broad streets, with neat one-family houses standing in the midst of well-kept gardens, representing the residential section in which are situated the American homes; on the other hand, we have the business section of the city in which sky-scrapers form the dominating feature. It seems that the inhabitants of even the newer American cities can not do without sky-scrapers. Each city must boast of at least one building which towers into the clouds, if it is only for the mere possession of it, even though there is no necessity, as in Eastern cities, for the existence of any such building. The snow-capped peaks of the Rocky Mountains to the North, Long's Peak and to the South, Pike's Peak, are visible from Denver.

To a great extent, Denver and its inhabitants are bound up with the mining and smelting industries of the Western States. Large machine shops are engaged in the manufacture of all the equipment necessary for mines, ore-dressing and smelting works. There are large plants for the supply of the laboratory requirements of mines and smelters, experimental stations for the examination of the ores of the West and the working out of methods for the conversion of ores, etc. In our visits to the plants of local industry we confined ourselves in Denver to the Globe Smelter of the American Smelting & Refining Co., the earthenware factory of the Denver Fire Clay Co., the factories of the Western Chemical Manufacturing Co. and the experimental station of the Henry E. Wood Ore Testing Co. The latter is used for the investigation of the convertibility of ores, their analysis, examination, etc. As far as questions of ore-dressing are concerned, this plant is somewhat similar (even though to a much lesser degree) to the experimental station for ore-testing of the firm of Humboldt, in Cöln Kalk and that of Friedrich Krupp-Grusonwerk in Magdeburg-Buckau, and like these it reports on the practicability of mining and smelting certain ores, and works out plans for these plants and their accessories. In addition, the station makes analyses of ores, and of the various intermediate products during ore-dressing and smelting, for small plants which are not in a position to maintain a laboratory of their own. It has special appliances for all processes of importance in Colorado: crushing



ores, wet concentration, the flotation process, magnetic and electrostatic ore-dressing, roasting, amalgamation, cyanid treatment and hyposulfite treatment, hence we did not see much of value in the factories of the Western Chemical Manufacturing Company, which especially prepares ammonia, nitric acid, sulfuric acid and carbonic acid in various grades of purity; but a short time before our visit it had suffered from a fire. Later on in the course of our trip we learned that shortly after our stay in Denver, the factory was burned completely to the ground. Although the factory was considered one of the most important in the West—for otherwise we should hardly have been brought there and shown through—it had little in common, either in outward appearance or interior construction, with a chemical plant such as we in Germany know it. Even though a part of the confusion and the dirt, etc. could be ascribed to the recent fire, that cause could hardly be held responsible for everything. I have often noted that in American factories, even those which are large, modern and in every way up to the mark, the same emphasis is not placed on cleanliness, order, etc. as in German plants. The high cost of labor is partially responsible for this condition. In order to keep a smelter or a factory reasonably clean, a large working force is required. In many parts of the United States, not only is this hard to obtain, but the cost is largely increased, so that it often happens that because of financial considerations the manufacturer places but little value on this work and finally becomes calloused and accustomed to the unsightliness of his plant. Similar observations could be made in many cities and localities; in an out-of-the-way corner could be found cars, material, etc., which had lost their utility. Though they made an unfavorable impression upon us who are so accustomed to cleanliness and order, there they lay and no one gave them a second thought.

THE DENVER FIRE CLAY CO. PLANT manufactures particularly ovens and containers for metallurgical and similar operations. It turns out ovens of different kinds and sizes, similar in construction to those built by German firms. Settling basins, cupolas, etc. are moulded and, in addition, it produces fire-proof bricks in various sizes and shapes. The ovens used for burning the fire-proofing materials are exceedingly simple in construction. In the evening, after dinner, the president of the concern, Mr. W. Case, was kind enough to take me through his plant and show me their extensive and elaborate stock-rooms for fire-proofed materials, and all the various chemical apparatus and appliances. From their warehouses in Denver and Salt Lake City, this firm, which is well known in trade circles, supplies the demands of the chemical and metallurgical laboratories of the West and of part of Mexico. I was glad to note that, being very particular as to the quality of the products they handle, this large firm supplies German chemicals exclusively—those of E. Merck, Darmstadt.

The presence, in the Rocky Mountains, of lead ores containing silver and of silver and gold ores, lays the foundation of the lead-silver-smelting industries in the interior of the United States. Lead is used as the collecting medium for the noble metals in all cases where the latter can not be recovered by the wet process, that is, in those cases where smelting has superior economic advantages over the wet methods of recovery. The most important silver smelters are situated in the neighborhood of Pueblo, Denver and Leadville, Colorado, as well as at Salt Lake City, Utah.

THE GLOBE SMELTER OF THE AMERICAN SMELTING AND REFINING CO. at Denver yields annually about 20,000 tons of sheet lead and about 2,400 tons of copper-lead pigs containing about 50 per cent copper. On the whole, Colorado ores (chiefly silicates) are converted, but in addition, lead ores from neighboring states such as South Dakota, Idaho, as well as the concentrates from the gold district at Cripple Creek are also converted. The limestone and the lignite, used as steam fuel, are mined

in the vicinity of Denver, while the coal and coke come from Trinidad, Colorado. The process is controlled electrically. All sulfid ores are roasted, except the slimes and concentrates from gold ore dressing and the rich Idaho ores. The roasting plant formerly consisted of 15 Freiberg furnaces, 2 Brown-O'Harra furnaces and 12 Brückner furnaces. An attempt was then made to replace this by a similar plant for the Huntington-Heberlein process, consisting of 8 round furnaces and 24 converters. Still later, the tendency has been to use the Dwight-Lloyd suction process. The plant now consists of various individual parts which give a most interesting perspective of the development and progress of lead-ore roasting. A small number of the Freiberg furnaces remain and are being used, not for lead-ore roasting, but for roasting lead pigs. For the purpose of roasting lead-ores there is in operation, in addition to the old plant consisting of the 2 Brown-O'Harra furnaces of the first plant, and a blast system (with several of well-known mechanical and a corresponding number of converters) of the Huntington-Heberlein process, a suction system according to the Dwight-Lloyd process, with its apparatus in the form of an endless chain. The Freiberg ovens are about  $60 \times 14$  and  $80 \times 16$  feet, respectively (outer dimensions) and each oven is run by one fireman and two roasters. The two Brown-O'Harra round furnaces, which have two levels, are about 90 feet long and are electrically controlled; connected with each is a small sinter oven for sintering the lead ores. Each oven has three firing holes along each length and each can roast 26 tons of ore to a 3 to 4 per cent sulfur content every 24 hours. As pre-roasters used in the Huntington-Heberlein process, however, they can handle 60 tons which they bring to a sulfur content of about 13 per cent.

Because of the silicious properties of the ore, no addition of silicic acid is required in roasting by the Huntington-Heberlein process, but instead there is an addition of iron to the ore. The round furnace for roasting by this process has a hearth 24.6 feet cross-section, a capacity of about 25 tons ore which is roasted to a sulfur content of 13-14 per cent. The oven is similar in construction to the puddling furnaces used in Germany; the round furnace was operated by means of a cog-wheel. The converters are situated in a ditch, with an area of  $13\frac{1}{2} \times 36$  feet and about  $10\frac{1}{2}$  feet deep, and they can be lifted up and carried away by means of cranes. The crane carries the converters to the filling hoppers (situated in front of the round furnaces) for hot and then for cold material; they are then brought back to their original position and connected with the blast. After the blasting process has been completed, the converter is once more brought by the crane to the emptying place and there it is emptied from a measured height so that the entire block is broken up into small pieces. The Dwight-Lloyd process consists of various apparatus in the form of an endless chain, a steel frame carries a loading-hopper, an ignition furnace, a suction tank and a pair of endless tracks for the accommodation of a train of little cars which, in the American literature, are known as "pallets." Each of these pallets has four wheels, by means of which it rests on the rails, and its bottom is in the form of a grate, where the ore to be roasted is placed. These pallets are joined to one another in such a way that they form a sort of endless, moving belt or conveyor on the tracks. Each pallet receives its load at the filling hopper. It then passes through the ignition furnace which brings the mass to a glow and starts the roasting process, and then, the still-glowing mass is carried on to the suction tank which is connected with a fan and here the process is ended. In passing through the suction tank, the bevelled bottom of the pallets slide over the bevelled walls of the suction tank, thus making this air-tight, as each of the connections between the various pallets themselves are perfectly air-tight. During the passage of the ore through the suction tank, air is sucked through the



roast and the ore, thereby bringing about the roasting of the ore. The pallet next passes through a "dead" area, which prevents the formation of air-holes in the suction tank. Thus the pallet finally reaches the end of the "road," there raised slightly by means of suitable apparatus so that the sintered parts are separated from the rest of the mass and broken off from the resulting substances. As the pallets slide over the cog-wheel (at the bottom), which causes the motion of the system, they become attached once more, are then brought to the lower end of the train, where they are once more attached to the other wheel, raised up and the cycle starts all over.

The suction system for roasting ores (introduced simultaneously by Dwight-Lloyd in America and F. v Schlippenbach in Germany) has several marked advantages over the blast process, such as continuous operation, the use of thin roasting layers (whereby, under certain conditions, a separate loosening appliance for the process can be dispensed with and the breaking up of the roasts obtained is simplified), and the prevention of the formation of a larger number of air-holes, which often happens in the blast process, either by the air employed or by the prolonged agitation of the bits of material which this air causes during sintering. Added to this is the possibility, in the models introduced by v. Schlippenbach in Germany, of easily obtaining about 60 per cent of the sulfurous acid in such concentration that it can be used for the manufacture of sulfuric acid. These sinters have pushed their way forward very rapidly in the United States and I saw them in use in practically every smelter I visited. The yield of such an apparatus is 50 to 100 tons according to the properties of the ores. At the Globe Smelter a number of blast-furnaces (made by the Colorado Iron Works Co.) are used for smelting the roasted material. Each has sixteen molds, about nineteen feet high and about  $0.4 \times 1.4$  inches. The air pressure is about 100-110 mm. mercury. Both slag and metal are emptied into large pots which are also made by the Colorado Iron Works. By means of an electric locomotive, these pots are brought to a reverberatory furnace (with a hearth area of about  $20 \times 12$  feet) where in masses of 14-15 tons the material is kept molten for several hours in order that a better separation of the various products may be effected. A little impure lead and a pig (which is emptied into a one ton cast-iron pan) are recovered from the slag in this furnace while slag, itself, which still contains 0.5-0.8 per cent lead and 0.0019-0.0021 per cent silver, is carried away in 5 ton pots and emptied in the yard. The metallic block obtained from the ore contains up to 10-12 per cent copper, 12-15 per cent lead, 0.14 per cent silver and 0.00017 per cent gold. It is broken up in a rolling mill, roasted in the above-mentioned Freiberg furnace, and then melted up in blast furnaces with 50 per cent copper; this material is later re-worked, in the Eastern States, for copper. The impure lead, while in a molten condition, is emptied by means of the stoking-hole of the blast furnace into 33 ton buckets, in which copper-containing scums are formed and drawn off. By means of steam forced in for ten minutes, the lead is well agitated and mixed for sampling and is then finally formed into bars which contain about 29 per cent antimony, 0.7 per cent silver and 0.025 per cent gold. This impure lead is then shipped East, where it is refined and de-silverized. The blast furnace gases are led through long, brick flue-dust canals to a filtering house containing 4000 cotton bags about 30 feet long by  $1\frac{1}{2}$  foot diameter. The gas supply is interrupted every six hours in order to shake the bags. The resulting flue dust is collected and re-smelted. The flue dust from the blast and roasting furnace canals are first sublimed in a small reverberatory furnace and finally in an arsenic sublimation furnace and obtained as a white meal—arsenious acid. Connorsville blasts are used for the blast furnace, two being No. 7 and two No. 8 blasts. Each blast furnace requires about 1275 cubic meters of air per minute.

#### CRIPPLE CREEK DISTRICT

From Denver we continued on our journey towards Colorado Springs, whence we made two side-trips, one to the Cripple Creek gold district and another, the ascent of Pike's Peak, by the cable road. We had the good fortune to see a most wonderful sunset from the latter point, at a high height of about 14,150 feet. The trip to the Cripple Creek district is a 50 mile ride through one of the most beautiful parts of Colorado. From Colorado Springs, at an altitude of 6,000 feet, the train gradually rises through a 40 mile stretch to Cameron, 10,466 feet above sea-level, and then descends for about six miles until it reaches Cripple Creek, 9800 feet above sea-level. As one rises higher and higher a most gorgeous view of the city is obtained and beyond this is the never-ending, rolling prairie which, in the distance, looks remarkably like the sea; this illusion is much strengthened by the shadows which, here and there, flutter across the horizon—smoke from some far-off locomotive, etc. The town of Cripple Creek lies in a mountainous country which is the result of ancient volcanic eruptions. The Cripple Creek lodes are practically gold ores with a small silver content. Free gold seldom occurs in the non-oxidized zone. The most important gold ore is Calaverite, a tellurium-gold compound which contains about 40 per cent gold and 1-3 per cent silver. At depths of over 100 feet, free gold is found, the greater part of which has been liberated from the tellurid. The ore occurs in very narrow lodes; the gangue occurs not only at the surface but remains unchanged at all depths reached and it has practically the same noble metal content as the lode proper. Pyrites is widely distributed both in the gangue and in the lode but it is often free of gold. Calaverite is, in every instance, the most important gold-carrier. The Cripple Creek gold lodes were discovered in 1891 and in the period from 1891 to 1901 yielded about 140 million dollars worth of gold. In 1906 the largest gold production took place, its value being about 20 million dollars. Ore is found even at a depth of over 1200 feet but the gold content decreases so that an increased gold production can hardly be expected from this district. The first ores showed great variations in gold content, the amounts ranging from 75 to 130 grains per ton. Formerly, open-working was the practice, but at present the ores are mined in shafts 1100 to 1300 feet deep. Those ores which are comparatively rich and will therefore bear the cost of transportation are sent, along with the pyritical concentration products from ore-dressing, to the neighboring lead smelters at Denver and Pueblo while the poorer grades of ore (having a gold content of \$2 to \$3 per ton) are recovered on the spot by means of the cyanid process.

STRATTONS INDEPENDENCE, LTD. PLANT—This plant is the most important one in the Cripple Creek district. Inasmuch as the properties of the gold telluride present in the Cripple Creek ores are very characteristic, the use of the ordinary methods for the recovery of gold presents many difficulties. The various methods of gold production developed in the course of the metallurgy of gold, from amalgamation up to the modern cyanide process and its modifications, have been used in the Cripple Creek district. Even the process recently discovered by Clancy for the electrolysis of ores in a solution containing atmospheric nitrogen, lime and potassium ferrocyanide has been tried for some time at one of the works—the Ajax mine at Victor. At the time we were in Cripple Creek, however, the process had already been abandoned, as it did not pay for cost of operation. At the present time the cyanide process is the one generally employed, but this is combined with concentration or some other supplementary method. The process in operation at the Independence Mill is substantially the following: A relatively coarse breaking up by means of stamp mills (Chilean) in the cyanide solution together with a very careful concentration of the material thus obtained, by means of which there is produced a high content concentrate and an intermediate product which

is then re-crushed and re-concentrated. The sand is treated by sprinkling and the slag by agitation with potassium cyanide solution, while the concentrates are sold to lead smelters, this being more economical than recovery on the spot on account of the high sulfur content. The substances containing gold telluride undergo another washing with cyanogen bromide. The potassium cyanide which contains the gold is precipitated by zinc flakes and this precipitate is sold.

The process used by the Independence Mill for the treatment of the most resistant gold ores has been worked out by Philip Argall. The plant established for this process can convert 10,000 tons of ore per month. The ore is in an enormous heap which has accumulated during the many years that the company has been in operation and has an average gold content of about \$3.75 per ton. It is to be noted that in the coarse crushing of ores it has been found that the resulting fine material is much richer in gold content than the relatively larger pieces; that is to say, the finest material contains the most gold. On the basis of this fact the entire crushing system of the plant has been installed. An effort is made to free the gold telluride as completely as possible in the crushing operation so that it can be readily separated by concentration and a sand obtained with a smaller gold content—say less than \$1 per ton—which can be easily extracted by means of potassium cyanide solution. The scum obtained which is rather rich in gold—about \$2 per ton—is concentrated as far as possible and then carefully extracted by means of potassium cyanide. The concentrates contain 0.15 to 0.22 per cent gold. After foreign material has been separated from the ore on a sorting conveyor, it is crushed in rollers to a fineness of about 36 mm. From the stock containers the ore (after first being washed with potassium cyanide solution) is brought to the mills in which it is further crushed and very intimately mixed with lime. It is next ground very fine in Chilean mills with the addition of a 0.02 per cent potassium cyanide solution which is added so that instead of a uniform scum there is obtained a finely divided product, admirably adapted for the ensuing concentration processes. A number of separators free the material from sand and this is then concentrated on hearths, resulting in a salable high content concentrate and an intermediate product which must be re-ground and re-concentrated. Marketable high content concentrators are again obtained, together with residues which have a very small gold content.

The scums are concentrated on Deister tables and vanners. The sand and the scum are parted in separators. The sand is washed in tanks for 4 days with a 0.02 per cent potassium cyanide solution and is then thrown away. All the scums from various parts of the plant go into settling tanks and then into washing vats in which, because of the high alkali content of the solutions, they are treated for six hours with a 0.03 per cent solution of potassium cyanide and then for 4 hours with a solution of cyanogen bromide. The gold solution is filtered *in vacuo* and then forced through filter presses. The precipitation of the gold is accomplished in the usual way by means of zinc flakes. The dilute solutions return to the concentration tables while the gold precipitate is dried and sold. The total extraction is estimated by Megraw<sup>1</sup> at 71.5 per cent, of which 43.6 per cent takes place in the concentrates and 27.9 per cent in the cyanide process while the consumption of chemicals is about 0.2 per cent of potassium cyanide, 0.12 per cent of zinc, 1 per cent of lime, and 0.18 per cent of cyanogen bromide. The cost according to Megraw is about \$1.30 per ton.

#### GLENWOOD SPRINGS AND SALT LAKE CITY

Leaving Colorado Springs on September 27, 1912, we traveled on throughout the day until we reached Glenwood Springs. This stretch proved to be one of the most beautiful trips we made in all our tour. We rode through the Garden of the Gods (near Colorado Springs) with its marvelous columns and pillars

of red and white sandstone, entry to which is gained by the gate of the Garden of the Gods, a narrow defile formed by two sandstone cliffs about 330 feet high. Beyond Cañon City we went through the great Cañon of Western Arkansas, a magnificent defile about 8 miles long and between whose perpendicular, towering walls, the foaming, turbulent Arkansas river flows. At the narrowest point, the Royal Gorge (at which place the train stopped for a few minutes), the enormous rocks tower to a height of more than 2600 feet. At this point the train crosses a bridge whose supports are lodged in the smooth walls of the cañon. On leaving the cañon the train follows along the course of the mad, on-rushing Arkansas. It was on this stretch that we were shown an arrangement which we Germans might well emulate. Before this beautiful locality was reached, an open car with seats was added to our train; from this we could enjoy the pleasures incident to observation of nature, with greater ease and facility than from our closed cars. Unfortunately, however, our enjoyment was the least bit marred by the large amount of soot, ashes and unburned coal which our powerful locomotive emptied upon our car.

GLENWOOD SPRINGS, a bathing place, is situated in a beautiful valley at the entry of the Roaring Fork into the Grand River. This bathing place is renowned for its hot sulfur springs. These have a temperature of 45–60° C. A stop-over of several hours gave us an opportunity to bathe either in the swimming pool, or in the bath-house or to enjoy a natural sweat bath in the hot (40–43° C.) vapor caves. From Glenwood Springs our train brought us on to Salt Lake City via Grand Junction, the Price River Cañon and the Wasatch Mountains Pass (at an altitude of about 7500 feet). Our train, unfortunately, was several hours late, so that in order not to delay the rest of the trip we were forced to dispense with part of our original program, the visit to the Garfield Smelters.

SALT LAKE CITY—A tour of this city and its environs acquainted us with the beauties of this spot which has been created anew from a barren desert through the efforts of the Mormons. By the aid of artificial irrigation, this sect (which, because of its polygamous tenets was compelled to migrate from the east) has transformed the parched and desolate region of the present state of Utah, on the so-called Great Salt Lake, into a veritable, fruitful paradise and thus has built itself a new home. This fact proves that, with sufficient water, this district makes an especially fruitful country, because the soil itself has the composition requisite for luxuriant vegetation. The stranger marvels much at the sight of this flourishing city situated in the midst of a barren waste and surrounded by naked hills on which practically nothing grows. There are many important and beautiful buildings in Salt Lake City. The large Mormon Temple and the Tabernacle are particularly worthy of mention. The large Temple, of gray granite, is about 180 feet long, 100 feet wide and its towers are about 213 feet high. Begun in 1853, it was completed only in 1893. The cost of construction was about 4¼ million dollars. The Tabernacle is a long, low building about 70 feet high and covers an area of about 250 by 148 feet. This building is used for the public gatherings of the Mormons and has space for 13,500 people. It contains the second largest organ in America, consisting of 3000 pipes and several hundred stops. We had the opportunity of listening to several pieces played on this organ. We shall long remember the masterful execution and the gripping effect of Handel's "Largo" and a Bach fugue which we heard on this occasion but the "Evening Song" from "Tannhäuser" was received with less approbation. In spite of the fact that we recognized the courtesy which was thereby shown us, the rendition of the "Wacht Am Rhein" received but little appreciation from us Germans because the organ is not adapted to this piece.

GREAT SALT LAKE—We visited the neighboring Great Salt Lake, which covers an area of about 16,000 sq. miles, as well

<sup>1</sup> Eng. and Min. Journal (1913), Vol. 95, p. 313.

as the Salt Gardens along its shores. Several rivers flow into this lake but it has no outlet and the excess water is removed only through evaporation. The lake is but a small residue of the prehistoric Bonneville Lake, which was a fresh-water lake until its waters lost their outlet. The periodically variable lake depth is, on the average, about 13 feet; about 3 feet in large stretches and about 39 feet in the deepest places. Very interesting information was advanced concerning the lake and its variable salt content. For a number of years, the salt content increased more and more since more water was lost by evaporation than was brought into the lake. As a natural consequence, the shores advanced further and further. In the period 1900 to 1904, it was even feared that the lake would disappear altogether. But from this time on, the level of the lake rose once more because of a very strong rainfall. In the last few years the salt content has once more decreased and the lake has become larger because during this time the relation between water addition and water loss is the reverse of that during the years from 1900 to 1904.

Year	Sp. G. of the brine	Solid content	Year	Sp. G. of the brine	Solid content
1850	1.170	22.28	1900	1.180	23.36
1873	1.102	13.42	1907	1.220	27.72
1889	1.157	19.55	1910	1.181	22.92
1892	1.156	20.51	1911	1.133	17.63

The lake has a minimum solid content in the spring of the year, this being slightly higher in winter but at a maximum in the fall. The solid content consists of 9.5-15.3 per cent  $\text{Cl}$ , 0.1-0.4 per cent  $\text{Mg}$ , 5.8-9.6 per cent  $\text{Na}$ , 1.0-1.9 per cent  $\text{SO}_4$ , 0.04-0.08 per cent  $\text{Ca}$ , 0.7-0.9 per cent  $\text{K}$ .

The Garfield Smelter is situated at the foot of a cliff on the shore of the lake. It is one of the largest copper smelters in the United States but, unfortunately, we were unable to visit it on account of lack of time. A bit of the smelter chimney was all that we saw of this large plant and from this such large quantities of smoke and soot poured forth that the remainder of the smelter as well as part of the neighborhood was completely enveloped. It was only because of this, that the presence of a large plant could be surmised. This picture of the smelter will certainly remain with every member of the excursion for it gave us a splendid idea of how the smelters of the United States formerly (and in some localities still do) worked without any consideration for the neighborhood, etc.

#### BAKERSFIELD, CALIFORNIA

On the day of arrival we left beautiful Salt Lake City; after a 24-hour journey over a distance of 868 miles through the barren and desolate wastes of the Mojave Desert into the state of California, we reached Bakersfield on the evening of the 29th of September. The following day, September 30th, was spent in visiting the oil fields of Bakersfield. This oil district is the largest in the United States. Of the total oil produced in the United States during the years 1912 and 1911, California produces a good third.

The production of natural gas in California is very small; it has an approximate value of \$800,000.

#### OIL PRODUCTION IN BARRELS OF ABOUT 300 LBS. EACH

	1911	1912 (estimated)
Total United States.....	220,400,000	220,200,000
California.....	81,100,000	87,000,000
Oklahoma.....	56,100,000	52,000,000
Illinois.....	31,300,000	28,000,000
Louisiana.....	10,700,000	10,000,000
West Virginia.....	9,800,000	11,800,000
Texas.....	9,500,000	10,500,000
Ohio.....	8,800,000	8,500,000
Pennsylvania.....	8,200,000	8,000,000
Indiana.....	1,700,000	1,200,000
Kansas.....	1,300,000	1,300,000
N. Y., Ken., Col., etc.....	1,900,000	1,900,000

#### SAN FRANCISCO

On the evening of Monday, the 30th of September, we left Bakersfield, reaching San Francisco, the most westerly point of our travels, on the morning of the next day. Three and a half days were spent in visiting this most interesting city. Like unto the fabled Phoenix, San Francisco has risen anew from its ashes and fragments since the great earthquake of 1906. But little remains to remind one of this cataclysm and only slight traces of the desolation can be seen. The city lies on the shores of San Francisco Bay and upon the hills which rise up majestically from its waters. From this point it stretches out over the entire peninsula on whose northern side is the Golden Gate—the entrance to the Bay—one mile in width. This city, together with its environs, boasts a wonderfully temperate, even climate which is somewhat similar to that of Southern France. The average temperature throughout the year is about  $14^{\circ}\text{C}$ . The picturesque bay, one of the most beautiful harbors in the world, is surrounded by a number of places like Oakland, Berkeley, Richmond, etc. It would have been very pleasant to tarry longer in San Francisco but it is also true that every one of the excursionists expressed the wish that we could have spent more time in California, both in Los Angeles and Pasadena as well as in this city. It was with heavy hearts indeed that we tore ourselves from this paradise.

Our reception and entertainment in San Francisco were most excellent, the program and its execution received the highest commendation from all the excursionists, so that we shall always look back with much satisfaction and joy to the happy hours spent in this and in other parts of the state of California. We had every opportunity for utilizing to the utmost the short time at our disposal for becoming acquainted with San Francisco and the most beautiful parts of its surroundings. In addition, a number of visits gave us an idea of the various phases of industry of this part of the country. A little trip to Muir Woods and to Mount Tamalpais took us for a ride over San Francisco Bay. From here is seen a beautiful panorama of the city itself with the Golden Gate in the east and Oakland and Richmond in the west. Landing on the northeast shore of the Bay, we passed through wonderful forests with tropical verdure, up to Mount Tamalpais, the top of which affords a most gorgeous view of San Francisco Bay and the surrounding country. From here a side-trip was made to Muir Woods and the Grove where we were amazed by several examples of the Sequoia gigantea and the Sequoia sempervirens (Redwoods) which have such enormous proportions, being 15 feet in diameter and about 200 feet high. On the return ride over San Francisco Bay (as well as on the next night) we had the good fortune of witnessing a marvelous sight—a sunset at the Golden Gate, an experience which had been vouchsafed but few of us before that time. The next day was spent in a trip to Berkeley, visiting the University of California. An auto ride from the steamer landing through the evergreens and gardens of Oakland's streets to Berkeley, gave us a view of this beautiful locality. The afternoon was spent in visiting the refinery of the Standard Oil Co. There is no necessity for going into any details on this plant as Prof. Holde,<sup>1</sup> described this fully from the verbal account of Dr. Erlenbach, one of the excursionists. The afternoon of the third day was devoted to a trip over the Bay to the works of the Selby Smelting and Lead Co., and to an inspection of this plant as well as the wine factory of the California Wine Association at Winchaven. No program had been scheduled for the morning so that the individual members of the tour were given an opportunity of either seeking a little rest from the fatigues of the journey or of undertaking little trips on their own account. The morning of the fourth day was devoted to a tour of the city and a trip to Golden Gate Park, the Cliff House and the grounds of the 1915 World's Exposition. In the afternoon, we left San Francisco, visiting the plant of

<sup>1</sup> Chem. Zeit., 193, pp. 53, 87.



the Leslie Salt Co. and Leland Stanford Jr. University at Palo Alto. From this point we continued on south to Los Angeles.

**GAS WORKS AT OAKLAND**—A report made by two of the excursionists who had an opportunity to visit the Gas Works at Oakland, was most interesting. To a great extent, petroleum is used for the manufacture of illuminating gas in California; lampblack and tar are by-products. In order to raise the quality of the lampblack (which contains tar and is otherwise used for boiler firing) the California Gas and Electric Corporation has introduced into its works at Oakland a process whereby lampblack is thoroughly mixed with crude oil and coked by a retort system. By means of the necessary generators, water gas is now produced at this plant from the lampblack resulting from the manufacture of gas from petroleum.

**CALIFORNIA WINE ASSOCIATION**—The German, who is accustomed to seeing wine produced from grapes with the greatest care in manipulation, is quite overcome by the operation of a California wine factory—this is the only name applicable to the process of making wine as it is practised there—as we saw it at the plant of the California Wine Association. This company converts practically all the grapes which grow in California, and the plant at Winehaven which we visited is the main one of this firm. The grapes go into the presses, etc., in car-load lots and in the operation of the factory, in fact to accelerate operation—working on the well known American principle of handling the largest possible quantity in the shortest possible time—the fermenting of the wine is hurried by an increase of temperature. While we in Germany require a relatively long time for this process, here the wine is finished in fourteen days. Naturally, California wine is not comparable to either French or German products. This fact is also due to another reason. In this heavenly climate the grapes, and all the fruits, grow to enormous size in a comparatively short time and ripen just as quickly. The result is that they become very sweet but lack the flavor of Rhenish or Moselle grapes. The wines which we tasted were somewhat similar in flavor to the white Bordeaux and Burgundy wines. California wine is used to a comparatively small extent in the United States as the American, when he drinks, seems to prefer German or French brands.

**THE UNIVERSITY OF CALIFORNIA**—The famous university at Berkeley met with the approbation of all the excursionists. A rather unfavorable impression, however, was made upon us by the student body with their military uniforms, equipment and drills on the one hand, and their non-military bearing on the other. It was plain to see that the weapon which the youthful student carried about with him was, to him, nothing but a toy.

**THE SELBY SMELTING WORKS** at Valeyo Junction lie on the northern part of San Francisco Bay (known as San Pablo Bay) on the shores of the water so that even larger sea vessels can dock at the plant. The plant is used, chiefly, for refining impure lead, and as a separatory for silver and gold. It is the largest and most important refinery in the west and possesses the advantage of being readily accessible both by land and by sea so that the products of the rich silver districts of western Mexico and of the gold districts of northern and western United States can easily be brought to it; hence, its gold and silver production is very considerable. European coke brought by way of the sea is used for smelting. Aside from this, oil-gas firing is used universally, in the distillation furnaces, for heating the steam boilers, etc. These boilers serve for the operation of the elevators and for the preparation of copper sulfate while the remaining power systems are electrically driven, the required current, at a tension of 9700 volts, being brought from a power house 160 miles away. The smelters are those of well known firms and do not vary from the usual models. The lead produced is 99.89 per cent pure. A part of this is used in the plant; a white lead and shot and cartridge factory in San Francisco is con-

nected with the smelter. The white lead factory works by the well known Dutch process.

The separation is accomplished by means of sulfuric acid, made in an adjoining sulfuric acid factory. The precipitation of the dissolved silver by copper, with the simultaneous production of copper sulfate, as well as the further manipulation of the silver, take place by the usual methods. The gases from the tanks being used for dissolving the silver alloys in sulfuric acid, are rich in sulfuric acid; they are freed from this by means of the Cottrell system. We were shown through this part of the plant and the appearance of the gases, both before entering and after leaving the Cottrell condensation apparatus, was called to our attention, so that we are able to realize the strong condensing action of the system. The Cottrell process precipitates fine bits of material, solid bodies like flue dust, etc., and liquid substances like sulfuric acid, out of gases by means of the electric current. The separation of suspended parts of gases by means of the electrical discharge, is, by no means, a recent innovation. Even in 1824, Hochfeld<sup>1</sup> proposed electricity as a means of suppressing ordinary smoke. In 1850, C. F. Gerillard made a similar proposal. O. J. Lodge experimented once more with the idea and the first tests on the commercial utilization of the principle were made by A. E. Walker, at the Dee Bank Works. Apparently, however, the system did not come up to expectations; it appears that the static machine used was at fault. About 1907, Cottrell took up the experiments of Lodge and succeeded in establishing a practical system for throwing down finely divided substances by means of the electric current.

The precipitation of suspended material from gases and liquids is facilitated by electricity either by the use of a direct or of an alternating current. The action of the alternating current consists in gathering together the suspended particles and thereby causing them to fall more quickly. Hence, the alternating current can be used to advantage on large masses of gases or liquids which remain perfectly stationary and in which a separation by gravity, etc., can be readily effected through a simple agglomeration of the suspended particles into larger aggregates. In the case of large masses of gases in rapid movement, *e. g.*, in the flue dust canals of smelters, etc., the conditions are altogether different and the direct current can be used. If a needle-point joined to one pole of a high-tension direct-current is placed in opposition to a plate joined with the other pole of the direct current, the air space between the two becomes charged with the same kind of electricity as the needle-point and isolated bodies brought into this air space become charged in the same way. If these bodies are free to move they will then be attracted to the oppositely charged plate by a velocity proportional to the charge and to the potential difference between point and plate.

In order that these experimental conclusions might be used practically, it was necessary to provide the high-tension direct current with a suitable source, and this problem presented certain difficulties. In the practical operation of the Cottrell process, an ordinary alternating current, such as is used for lighting or power, is transformed into a similar current at a tension of 20,000 to 30,000 volts and this high tension alternating current is commutated into an intermittent direct current. This current is then used on a system of electrodes in the canals through which the gases in question must travel.

Although the preparation of the plane electrodes presents no untoward difficulties, the same can not be said of the construction of the discharge electrodes. In the former case practically any flat conducting plate can be used. From experimental observations, the use of a cotton-wound wire as discharge electrode at ordinary temperature was decided upon as it was found that

<sup>1</sup> THIS JOURNAL (1911), Vol. 3, No. 8. F. G. Cottrell, "The Electrical Precipitation of Suspended Particles." For this account I am under obligations to Moeller and Brackwede, who are interested in the pertinent patents and control the German rights to the process. See German Patent 230,570, *Chem. Ztg. Repert.*, 1911, p. 84.

this gave much better results than the system of metallic points heretofore employed. Asbestos or mica is used for the hot acid gases from smelters, and in this case the fine threads or the thin flakes, respectively, form the discharge points. These are so attached to the wire that they form the conductors for the current when moistened by the condensed water or acid vapors. The first practical tests of the Cottrell process were made in 1906, at the Hercules Works of the E. I. duPont de Nemours Powder Co. at Pinole, on San Francisco Bay, with the gases from their Mannheimer contact sulfuric acid plant. It was because of these tests and their results that this problem was attacked at the Selby Smelter. A plant for the Cottrell process was installed for the gases from the dissolving tanks of the gold and silver separators. Several rows of lead plates with a surface area of about 4 in.  $\times$  4 ft. are placed in the 4  $\times$  4 ft. lead canals approximately four inches from one another. Between each pair of lead plates is hung a leaded iron rod which bears the mica. The 460 volt smelter current is transformed to 1700 volts and is then brought to the electrodes by means of a synchronous equalizer. The energy required is about 2 kilowatts. The process, which has been in use for 4 years, gives good results. We had an opportunity of again seeing a Dwight-Lloyd system of roasting in operation, at the Selby Smelter. This system was provided with the necessary loading devices (automatically controlled), silos, conveyers, etc.

**LESLIE SALT CO.**—The salt farms of this company at Leslie, near San Francisco, afforded us a most interesting view of the process by which salt is recovered from sea-water along the shores of the Pacific Ocean. The water is pumped from the ocean and allowed to evaporate in so-called sea-gardens by means of solar heat. Each acre of the salt gardens yields about 400 tons of salt annually. The salt is brought by a conveying worm to a large heap where it is allowed to remain until it can be further worked. By means of water, it is separated and dissolved from the heap and this solution is then evaporated in a three-fold vacuum system with continuous operation by means of elevators. The salt is used mainly for technical purposes.

**LELAND STANFORD JR. UNIVERSITY** was founded by Mr. and Mrs. Leland Stanford in memory of their only son. It has an endowment of about 30 million dollars and was first opened in 1891. It has law, philological and scientific faculties, as well as an engineering department. A remarkable impression is produced by the magnificent buildings of light brown sandstone surrounded by oak and eucalyptus trees and the yard of the older college buildings with their pillared halls, in which yard an almost tropical vegetation holds sway. There is also a splendid library of about 110,000 volumes and an excellently equipped and much used reading room.

#### LOS ANGELES

We traveled along the coast of the Pacific Ocean to Los Angeles which we reached at about noon on Saturday, Oct. 5th. This exceedingly flourishing city lies on the slope of the Sierra Santa Monica, being shielded by this from cold winds. The city lies in the midst of a veritable paradise of gardens, vineyards, fruit and olive groves. Los Angeles is the emporium for the famous California fruit-growing industry. Pleasing tropical vegetation abounds on all sides. Eucalyptus, spice bushes, palms, evergreens, orange bushes, roses, geraniums, yuccas and pomegranate trees flourish in remarkable profusion and delight the eyes of the onlooker. Los Angeles owes this remarkable development of fruit growth and this wonderful wealth of plant life to the happy combination of two circumstances. First, there is its protected situation in the warmer district of artificial irrigation; second, by means of enormous artificial water conduit it is possible to bring in an abundant water supply. Without this, this flourishing vegetation would not be possible for it often happens that not a single drop of rain falls for many months. The water conduit comes from a distance of about 250 miles

and the quantity of water thus brought approximates one million cubic meters per day. From the fall of this water there is obtained, at the same time, a force of about 120,000 horse-power. This magnificent system of irrigation, together with the warm climate and the fortunate situation of the district, has created a paradise which the traveler leaves only unwillingly. Unfortunately the duration of our visit was very short so that we could devote but little time to the enjoyment of this magnificent neighborhood. A wonderful trip by electric railway to Long Beach, a bathing resort on the Pacific, showed us the beautiful districts which lie east and south of Los Angeles. Our further tour of the coast was prevented in a most unpleasant way by a collision with a freight train. Fortunately none of the excursionists were injured so that, after our demolished car had been removed and another substituted, we were able to continue our return to Los Angeles and a trip to Pasadena which lies north of that city. Late in the afternoon we visited the laboratory (now in course of construction) for the Observatory on Mt. Wilson which is situated at this point. An interesting illustrated lecture by Prof. Hale acquainted us with the equipment and work of this observatory, which possesses the strongest telescope in the world, a mirror telescope with a diameter of 63 inches.

#### RIVERSIDE

**RIVERSIDE PORTLAND CEMENT CO.**—Only too quickly our train carried us further through orange groves, fertile orchards and magnificent country on to Riverside, a booming town, which boasts gardens and streets with the most luxuriant vegetation. Here we interrupted our journey for a few hours to visit the plant of the Riverside Portland Cement Co., which, on account of an installment of the Cottrell process, was of great interest. The cement factory has a daily capacity of about 900 tons; it contains 10 ovens. The Cottrell system was inspected under the able guidance of Mr. Schmidt of the Western Precipitation Co., chemical engineers of Los Angeles. The cement factory was compelled to install a system for the condensation of the fine cement dust, as the near-by orange groves upon which this was precipitated were injured by this substance. The plant, which cost about \$100,000, is very efficient. It yields, as a by-product, a fine dust which may find use in fertilizers as a substitute for potash salts. Experts, however, doubt the claims which Americans make in this regard.

#### ARIZONA

**GRAND CAÑON**—Our special train took us from the California wonderland through barren districts into the state of Arizona, where we were able to see one of the most magnificent and interesting bits of scenery in the United States, the Grand Cañon of the Colorado River. On this trip, unfortunately, we lost a full day of our tour which we had to make up later. This we did by omitting our trip to Sulphur, La., by which, however, we did not lose so very much since the Union Sulphur Co. (whose plant was the most important one we could have seen in Sulphur) had withdrawn the permission originally accorded us for the inspection of their factory for the recovery of sulfur by the Frasch process. On our trip to the Grand Cañon that derailment of our train took place, of which I have already spoken. This railroad accident was caused by an almost unbelievable occurrence, an undermining of the road which gave way under the load of the train, while the poorly fastened rails were loosened from the ties. That we came through this derailment safe and uninjured was due solely to the fact that the train was running along at a diminished speed on account of an up-grade. A relief train was on hand after the lapse of a comparatively short time; locomotive and derailed cars were put back on the tracks while we ourselves continued on our journey in a second relief train. As our special train had to be made up again, and, in addition, the rails put into condition for carrying traffic, a full day was at our disposal which we were able to spend in a visit to the Grand



Cañon. The majority of the party on mules and horses, three of us afoot, made a tour through the Grand Cañon to the Colorado River and back which distance we covered in nine hours (including stops) making a round trip of about seven miles and a total altitude of about 4000 feet. The Grand Cañon of the Colorado is one of the most wonderful sights in the world; in the direction of the river it is about 220 miles long while measured from wall to wall it is 8-10 miles wide and has a depth of 2800-4900 feet. The 280 foot wide Colorado, which, when the water is high, becomes swollen to a depth of 230 feet, forces its way through this cañon, eating further and further into the surface of the soil. This enormous gorge has been formed by the action of the turbulent waters and shows the curious traveler all the formations from Cambrian to Tertiary from which the corroding influence of the waters has carved numberless cliffs and peaks. In wandering through this valley one is amazed by the brilliancy of these layers which glow wonderfully with the most varied colors. In the upper portions of the ravine can be seen massive layers of light gray limestone to which, at lower levels, are joined red and white bands of sandstone, dark red limestone, dull gray slate, dark brown quartz and red granite.

After our train had come to Grand Cañon station, we left the Grand Cañon on the evening of Thursday, Oct. 8, 1912, and proceeded through Adamana, Arizona and Albuquerque, New Mexico, to El Paso, Texas. At Adamana, on the borderline of Arizona and New Mexico, we interrupted our journey in order to visit the Petrified Woods or Chalcedony Forests of Arizona, situated about seven miles south of this point. By a rapid journey, in a rocking, double-teamed coach through trackless sandy wastes and completely dried up river beds, we reached a district occupying an area of thousands of acres in which there were scattered countless tree trunks 30 to 100 feet long (silicified to depths of 3-10 feet) of *Sigillaria*, *Lepidodendron* from the Triassic Age, and *Dadocyles* partly buried in marl, and in other places washed free from this by wind and rain. Some of these petrified trees are over 190 feet long and more than 10 feet in diameter. Such a tree trunk, 100 feet long, which was not broken by its fall, forms a natural bridge over a ravine.

#### MEXICO

We made a stop-over of several hours in El Paso, the border-town between the United States and Mexico, which is situated on the Rio Grande del Norte, in order that we might make a little trip to Juarez, the Mexican town on the other side of the border. The insurrection of President Madero (who was later shot) started here and evidences of the heavy fighting which took place at that time could be seen everywhere on the various buildings and especially on the churches. Both the inhabitants of the place and the Mexican army made a rather unfavorable impression upon us and it can readily be understood that the government of the United States keeps a large body of troops both at El Paso and along the boundary line which the Rio Grande del Norte forms for quite a stretch in order to prevent the entry of bands of Mexican bandits into the territory of the United States.

#### TEXAS

In order to reach Fort Worth, Texas, our next stop, we then traveled through the state of Texas, arriving at our destination on Friday morning, Oct. 11, 1912. On this trip we rode through wide stretches of country which the Americans have recovered for agricultural purposes by means of artificial irrigation. By this means the dry plateau of Leano Estacado, to the north of the railroad and covering an area of about 50,000 square miles, which originally was covered with only cacti and barren shrubs, has been converted into a large cattle pasturage. In contradistinction to California where the water is brought in large conduits from the mountains, here the water must be procured by means of pumps from the ground-waters which are at a

depth of 15 to 20 feet as this district is non-mountainous. The result, however, is the same as in California. The irrigation results in an enormous development of the agriculture of this locality and we marvelled much at its products, which we were able to see at an agricultural exposition in Pecos which we visited during the two-hour stop-over at that place. Wool and cotton are, naturally, the products of this re-claimed territory. The fertile meadows of the state of Texas lend themselves readily to cattle raising so that Texas has naturally developed into one of the chief cattle-producing states of the Union. Large branches of the Chicago slaughter-houses of Swift and of Armour have been established in Fort Worth. We did not visit these plants as we had seen the similar ones in Chicago. However, we saw the operation of several processes for the further conversion of various slaughter-house by-products. Then followed an inspection of the methods of preparing "butter" from the fat of slaughtered hogs and from cotton seed oil, which is recovered on the spot. Moreover, at these plants, we saw the conversion of meat and slaughter-house residues into meat meal which is used in the preparation of artificial fertilizers (a process we inspected in the corresponding plants of Armour & Co. at Atlanta). We next visited a corn elevator, with silos, a cotton-gin to which is attached a plant for separating the oil from the cotton seed, and finally several plants for pressing and packing cotton

#### LOUISIANA

On Saturday morning, Oct. 12, 1912, we reached Shreveport, La., a bustling commercial and manufacturing town which has become famous of late on account of its wealth of petroleum and natural gas.

THE CADDO OIL FIELDS, near Shreveport, were opened recently and are also very rich in natural gas. This district forms the richest gas field in the United States. In the recovery of both oil and natural gas, the Caddo Fields have been but partially developed. Although the existence of this natural treasure had been known for years, it was only in 1906, that both oil and natural gas were recovered in considerable quantities. The two kinds of wells occur together. The practical gas wells are bored at an average depth of 1000 feet and the pressure at the beginning is 500-1000 lbs. per sq. inch, which remains practically constant. The daily stream of gas from these wells varies from 5-10 million cubic feet for each. About 16,000 cubic feet of Caddo natural gas are equivalent to a ton of coal. We were told that the United States Geological Survey has shown, after careful investigation, that it would be possible to produce electricity in large quantities with a constant maximum utilization, in Shreveport, from Caddo natural gas at 15.6 cents per 1000 ft. cheaper than it can be produced by the electric plant at Niagara Falls, by the use of water power. Caddo natural gas contains 95 per cent methane, 2.56 per cent nitrogen, 2.34 per cent carbonic acid and 0.01 per cent hydrogen, no carbon monoxide, no acetylene. The gas is piped to Shreveport and other places. For household purposes, the gas is sold in Shreveport for about 23½ cents per 1000 cu. ft.; but for industrial uses the rate is from 4½-8½ cents per 1000 cu. ft. In the course of the few years it has been in operation, the oil production of the Caddo Fields has developed enormously. While in 1906, only 3358 barrels were produced, the yield in 1911 had jumped to 6,995,828 barrels (of about 40 gallons each). In this district the petroleum is obtained at an average depth of about 2300 feet. The field is noted for its large gushers which occur from time to time. One of the wells produces 72,000 barrels of oil a day, while wells which produce 15,000-25,000 barrels daily are common. The white oil has a gravity between 41° and 43° B. which corresponds to a density of 0.8187-0.8092. The Standard Oil Co. transports the oil to its refinery at Baton Rouge. The refineries of the Texas Co. are at Port Arthur and those of the Gulf Refining Co. are at Beaumont and Sabine, Texas. Three other companies have plants at Shreveport. The railroads use



a good deal of the petroleum as fuel for locomotives. The price of the oil is about \$1.05 per barrel. The price is dependent upon the freight to the place where it is sold. About  $3\frac{1}{2}$  barrels of crude petroleum are equivalent to a ton of coal. The Shreveport Gas, Electric Light and Power Co. sells electric power at a cost of  $8\frac{3}{4}$ - $5\frac{1}{2}$  cents per Kilowatt-hour, depending upon the number of hours. It is to be noted that large quantities of lignite (which is mined in Western Louisiana and eastern Texas—this bed is the largest lignite bed in America) can also be obtained so very cheaply that the generator gas produced from it can compete with the natural gas. Shreveport is also a cotton center and enormous quantities of cotton are prepared for distribution in the local presses. During each harvest period, 300,000 bales of cotton weighing about 900 pounds and having a value of 16-22 million dollars pass through this district. The three local cotton presses can bale about  $\frac{1}{2}$  million bales of cotton.

We had numerous opportunities of inspecting gas and petroleum wells. One of these was particularly interesting because it showed how often the Americans still are reckless and extravagant in the treatment of their rich natural resources. From its history we could also see how laws which do not meet with the approbation of the parties concerned are frequently violated in America. We were shown a well which was bored in 1906-1907. Water forced an entry into this well and at the same time the plant was destroyed by a cyclone. From the mouth of this well there poured forth a mixture of water and gas in the form of a geyser 15-20 feet high into a pool thus formed about the mouth, but the well was simply abandoned. After a sufficient number of visits and photographs of this exhibition had been made, the geyser was intended in order to show the quantity of gas which pours forth here unutilized. The burning lake with its burning geyser, makes a wonderful picture but oh, what quantities of valuable gas are being lost! The government has even had an expert look into the question of the well and its seizure; a law has been passed that the well be locked but this is not enforced and the gas is still being lost. In order that we might see the enormous pressure with which the gas issues from the wells, a well at Lewis was opened which yields 30,000 cu. ft. of gas per day. With a terrifying, shrill shriek the gas rushed out of the conduit in a high stream far over the roof of the building.

#### NEW ORLEANS

The trip planned to Sulphur, La., for the inspection of the plant of the Union Sulfur Co., was given up for reasons already mentioned and so, once more according to schedule, we arrived on the morning of Sunday, Oct. 13, 1912, at New Orleans, which was the southernmost point of our journey. This city, in itself, presents much of interest and we got an idea of its beauties and characteristics by means of an auto trip around town. On the whole, the newer parts of the city are similar to all the newer cities of the United States. The many private mansions bear witness to the fact that many people of wealth and many captains of industry have taken up their abode in this very beautiful city. In many ways, New Orleans is one of the most interesting cities of the United States for there remain many evidences of its French and Spanish occupation, not only in the undisturbed existence of entire quarters but also in many of the customs and habits of the town. The forenoon was spent in a visit to the municipal water-purification plant (which must purify 40 million gallons of water for the city) but, unfortunately, the trip which we had planned down the Mississippi to the Gulf of Mexico had to be given up on account of the inclemency of the weather. In the evening we left New Orleans to continue in a northerly direction on our travels through the states of Alabama, Georgia, Tennessee, North and South Carolinas, etc., before we once more reached the starting point of our tour.

#### BIRMINGHAM, ALABAMA

The first station on this trip was Birmingham, Alabama, which was reached on Monday, Oct. 14th, after a considerable delay. These delays which our train suffered made themselves uncomfortably prominent and in addition had an appreciable effect upon our original plans. However, it must be said, that the delays we experienced were quite negligible when compared with the delays which regular trains must undergo. A number of distributing factors had considerable influence on the carrying out of our Birmingham program so that we were unfortunately compelled to curtail our trip through the Birmingham district, in which so many industries have found a home. But in spite of all this, our tour was very instructive and our worthy hosts made every effort to make matters perfectly clear and comprehensible by explanations of all kinds. Birmingham is a beautiful, modern city, being only 39 years old. It is the center for a very considerable iron industry. The wealth of the natural resources of this locality is almost fabulous while enormous iron works, coal mines and various other industrial plants tend to make the city one of the most important of the South. The natural resources are of such a nature as to bring about the development of an important iron industry. The quality of the ores is such that they can be converted by themselves without the addition of any foreign ores in the smelting. Red and brown hematite, coal (which can readily be coked), limestone, and dolomite (both of excellent quality) occur in abundance and a good pig iron can be made in this neighborhood easily and cheaply.

ENSLEY, which is the largest industrial center in the Birmingham District, was the place chosen for particular observation. There are located the mines, coke-ovens, blast-furnaces, steel mills, rolling mills and machine shops of the Tennessee Coal, Iron and Railroad Co., the coke ovens of the Semet-Solvay Co., the plant of the Barrett Manufacturing Co. (manufacturers of roof-coverings), a branch factory of the Fire Brick Co., etc. The blast furnace system of the Tennessee Coal, Iron and Railroad Co. consists of 6 blast furnaces, with an annual capacity of 640,000 tons of pig iron. The steel works comprise 8 reverberatory furnaces (of 100 tons capacity) and 2 converters of 20 tons. The rolling mills include both plate and rail rolling mills. The latter has an annual capacity of 400,000 tons. Although the ores are too low in phosphorus content and too high in silica to be adaptable for the Thomas process, the phosphorus content is, nevertheless, sufficiently high so that it is possible to prepare a suitable molten iron for the acid converters. For this reason there are, in use, acid converters (in which the iron is dissolved and freed of silica) as well as basic Martin ovens (in which the iron is completely decarbonized and freed of phosphorus by treatment with ores containing iron oxide, hematite and lime. Thus the oxidation of the pig iron is accomplished by means of the oxygen of the ores). At Ensley we were able to visit an absolutely new coke oven plant built by the Koppers system with recovery of by-products. From both a technical and an economic point of view, the production of coke in the United States is, as a rule, at a rather low stage of development. As was previously mentioned, in the discussion of Pennsylvania, the greater part of the coke is still being manufactured in the antiquated bee-hive ovens no longer employed in any part of Germany. These ovens (which, with a diameter of 13 feet are 7-8 $\frac{1}{4}$  feet high) are, naturally, combined in batteries. An opening in the roof serves to load them while an opening in the side-walls is used for emptying. Of late, the process of loading is accomplished through the use of large electric cars which move above the ovens. The coal is distributed either by hand or by appropriate mechanical devices. The emptying, particularly in localities where cost of labor is relatively high, is also done by mechanical means, and on account of the round shape of the oven the apparatus for this purpose is rather complicated

in construction. On an average the feeding time for blast-furnace coke is 48 hours. The output of the bee-hive is poorer than that of the by-product ovens. In the first place, the average yield is less and secondly, there is a total loss of all the by-products [such as tar,  $(\text{NH}_4)_2\text{SO}_4$  and benzol] which, in Germany, are recovered from coke and the coke oven gases. In the United States, by-product ovens are being introduced only gradually. Since H. Koppers, in 1908, erected the first plant for the operation of the system which bears his name for the Illinois Steel Co., at Joliet, many Koppers ovens have been installed. In the account of our visit to the Gary Works, I gave a brief description of such a plant. The coke oven plant (Koppers system with recovery of by-products) which we visited at Ensley consists of 4 batteries of 70 regenerating furnaces, three batteries being in operation. Each oven converts about 15 tons every 24 hours so that the total capacity of the 3 batteries is about 3000 tons per day. The feeding time is 21–22 hours. At the time of our visit, the by-product recovery system recovered only the tar and the ammonia (the latter by the direct Koppers process) but there was in course of construction a plant for the recovery of benzol, for, as we were told, about \$3000 worth of this substance is uneconomically consumed each day in the combustion of the gas in the gas machines. A splendidly equipped system for the recovery of by-products was planned for the conversion of the gas from 560 ovens; that is, from 8 batteries of 70 ovens each.

AMERICAN CAST IRON PIPE CO.—Late in the evening, after we had returned from our trip, we were shown through the pipe foundry of the American Cast Iron Pipe Co. by the president of the concern. This plant is located near Birmingham. As he himself told us, we owed the hearty and courteous reception which the president accorded us to the splendid treatment which two of his employees (who, in the preceding year had been to Germany to study German pipe-foundries) had received at the hands of the German firms in this line. To the spectator, the operation of the factory in the late hours of the night presented a most wonderful subject for a painting by an artist who wished to portray the picturesque process. The electric lights shone but dimly through the vapor mists, here and there the black forms of the workmen (who, in the main, were negroes) appeared but as dark shadows fluttering to and fro through the hazy clouds; between these the molten iron (which was flowing from the cupola) glimmered and glittered; added to this came the loud cries of the drivers (horses are used for transportation of material to the various parts of the plant), the shouts of the workmen, and the pounding of the moulders. This factory employs 500 workmen and produces 240 tons of pipe per day,  $\frac{2}{3}$  being produced by the day shift and  $\frac{1}{3}$  by the night shift. The iron is melted in four cupolas, two of which have a capacity of 10 tons each per hour and two a capacity of 14 tons each per hour. We had an opportunity to observe the strained relations which, in the locality, exist between employer and employee. Although the laborers received, on the whole, rather courteous treatment from the president, still it must not be forgotten that the colored laborer is just as good a man as his employer and, if he becomes dissatisfied with the treatment accorded him, he simply leaves, thus bringing about a very unpleasant situation, for shortage of labor reacts very disturbingly upon the operation of a plant. Because of this condition, the molding of pipes varies in two respects from German foundry practice. In Germany, the pipe is poured standing in such a way that the flange is underneath while in America the opposite is true; the pipes are poured standing so that the flange is above. In this way, the work is facilitated and simplified. Then again, the wall-thickness of the pipes is greater than in Germany for, on account of poorer moulders, all molded material is formed much thicker. It is impossible not to draw the conclusion that negroes are not adapted for moulders.

## ATLANTA, GEORGIA

On the evening of the same day we left the highly interesting and hospitable city of Birmingham and on the next morning reached Atlanta, Georgia. Atlanta, the capital of Georgia, with a population of 175,000, lies on the water-shed of the southern coast of the Atlantic Ocean and the Gulf of Mexico at an altitude of about 1000 feet above sea-level. It is the industrial center of the southeastern states for railroads, banking, commerce, etc.

THE ARMOUR FERTILIZER WORKS at Atlanta were visited. This factory makes a mixed fertilizer with 2 per cent nitrogen, 2 per cent potash and 10 per cent phosphoric acid by combining slaughter-house refuse (the conversion, meal and grinding of which we saw at Fort Worth, Texas) with superphosphate which is manufactured in Atlanta. The plant includes a sulfuric acid factory, with 24 gravel burners and 180,000 cu. ft. volume chamber, in which about 50 tons sulfuric acid are produced daily. The phosphoric is ground in Kent Mills, then mixed in an iron mixing tank by agitation with a measured quantity of acid (lead measuring tanks are used) and then comes to a wooden chamber lined with brickwork. The resulting superphosphate is then combined with the animal refuse and forms the mixed fertilizer in question. Although the principle of such a fertilizer for agricultural purposes has its advantages for the manufacturer, it has distinct disadvantages for the farmer who would prefer that a fertilizer be prepared which takes into consideration the varying requirements of different soils. After an official reception by the Governor of Georgia, at the Capitol, Prof. McCallie of the Geological Survey gave us a most interesting, illustrated lecture on the mineral wealth of Georgia.

## DUCKTOWN, TENNESSEE

The next day was spent in visits to the copper smelters of the Tennessee Coal and Iron Co. and the Isabella smelters of the Ducktown Sulfur, Copper and Iron Co. at Ducktown. Ducktown is a small place in the Tennessee mountains but it is the seat of the main works of the Tennessee Coal and Iron Co. A pyrites which contains about 2 per cent copper is converted in this district. The ores (which are rich in sulfur) are melted in blast furnaces to copper without the addition of coke. Both the iron and the sulfur serve as the heating material, the former burning to ferrous oxide (which is slagged) and the latter to sulfurous acid (which goes over in the blast furnace gases). From purely practical considerations, a slight addition of coke is made. Naturally, the conversion of large quantities of an ore so rich in sulfur causes the simultaneous evolution of considerable quantities of harmful gases to the detriment of neighboring agriculture and forestry. On this account, both smelters which convert the iron were compelled to attack the problem of making the acid blast furnace gases perfectly harmless, a problem which had not, up to that time, met with successful solution. The aim is to convert the hot blast furnace gases (which contain both carbonic acid and flue dust) to sulfuric acid. Both works have solved this problem with the greatest success. The manufacture of sulfuric acid which was first undertaken from necessity has now become a source of income for both plants. The preparation of sulfuric acid from the gases in smoke can be pursued to advantage only where there is a market for this substance and, fortunately, this is true in this district. A very important industry has been developed in the south—the manufacture of artificial fertilizers—which requires large quantities of sulfuric acid. The entry of the Tennessee Works, with their enormous production, into the manufacture of sulfuric acid had a deleterious effect on the traffic, particularly the importation of pyrites into the United States, and at one time the worst was feared in this direction. But the manufacture of fertilizers is steadily increasing and the two works control the sulfuric acid market for only the southeast of the United States, while for remoter localities they do not come into consideration at all as pyrites



competitors, because the latter can be transported much more readily than sulfuric acid. In their own field, however, these plants have an excellent market for the enormous quantities of sulfuric acid which they produce.

**THE TENNESSEE COPPER CO.**—The plant of the Tennessee Copper Co. was begun in 1906, completed in 1907 and put into operation in 1908. At this time the estimated total production of the plant was 110,000 tons of 60 per cent acid per annum. In 1910 the plant was enlarged so that now the estimated capacity is 160,000 tons and the actual production is 180,000 tons. The plant is one of the largest sulfuric acid factories ever built. It consists of two octagonal Glover towers 50 feet high and 30 feet in diameter with the appropriate saltpeter furnace at their base, a canal  $10 \times 20 \times 120$  feet from the Glover towers to the cooling chambers, 16 cooling chambers  $10.7 \times 10.16 \times 70$  feet; 8 cooling chambers  $10.7 \times 20 \times 70$  feet, 4 Hart lead ventilators with a capacity of 1900 cubic meters gas per minute, 12 lead chambers  $50 \times 50 \times 70$  feet, 6 lead chambers  $50 \times 50 \times 72.4$  feet, 8 lead chambers  $23 \times 50 \times 80$  feet (these chambers with a total chamber volume of  $4\frac{1}{2}$  million cu. ft.), 4 Gay-Lussac towers  $23 \times 23 \times 50$  feet high, 4 octagonal Gay-Lussac towers with a diameter of 19 feet and 20 feet high and 2 octagonal Gay-Lussac towers 36 feet in diameter and 65 feet high. To these are added the requisite acid coolers, acid pumps, acid carriers, etc. and 15 storage tanks with a capacity of 15,000 tons of acid. There were required for the building of the plant, 4650 cubic meters asphalt for the foundations of the chambers,  $4\frac{1}{2}$  million bricks of various kinds for the canals and unions, 8000 tons quartz (sand) for the filling of the towers, 225 tons asbestos for insulation of the canals and 3600 tons lead for construction chambers, towers, etc.

Because of the kind of chamber used, the construction of the sulfuric acid factory is of interest. The chambers were built according to the Falding sulfuric acid system. Since, in the formation of sulfuric from sulfurous acid, there is a liberation of heat and because of this the hot active gases tend to rise to the top of the lead chambers while the cold gases (which no longer enter into the reaction) tend to sink to the bottom, these chambers are so constructed on the Falding system that they are higher than they are long and the relation between the height and the length is proportional to the volume of the gases. In chambers longer than they are high, the chief reaction occurs where the gases enter while no reaction is manifest at the other end of the chamber, and remixing of the gases is necessary for starting the reaction once more in the further chambers. It should be possible, in the Falding system, to bring the reaction to a complete development in a single narrow, but exceedingly high, chamber, so that all the sulfurous acid will have been removed from the gases which leave this chamber. The works of the Tennessee Copper Co. bear testimony to the fact that this is not always feasible, for it has been found necessary to put up a series of these chambers in order that all the sulfurous acid may be transformed to sulfuric acid. The chamber walls are so suspended from lead beams that at no point can steel and lead come into contact with one another. This enormous plan has solved the problem of converting large masses of highly heated gas charged with flue dust, large and variable quantities of carbonic acid (resulting partially from the ores and partially from the coke and the limestone of the blast furnace loads), which pour forth from the blast furnaces in variable quantities, into sulfuric acid. The blast furnaces which are used for melting the pyrites have been altered in such a way that they furnish a uniform flow of gas. The furnace mouth is so arranged that no mixture of furnace gas and outside air can take place. The blast furnace gases are led through an enormous flue-dust chamber  $25.3 \times 36 \times 163$  feet. This chamber has iron wires to effect as complete as possible a separation of the flue-dust, while, at the same time, the chamber serves to maintain and

regulate the temperature of the gases and delivers these to the Glover-tower at a uniform temperature and pressure. By means of an appropriate, large gas conduit the gases are then brought to the Glover tower and from these, for further cooling, to a system of tower-like cooling chambers (of lead) so that they may be sufficiently cool to enter the chambers. In the Glover towers the acid is carried by means of acid carriers—large lead buckets which are raised and lowered electrically. The plant produces about 140,000 tons of 60 per cent sulfuric acid at a cost of less than \$2.40 per ton.

The Tennessee Copper Co. converts about 400,000 tons of low-grade copper ore mined partly in open workings and partly in shafts. The ore is 75 per cent pyrrhotite and a little pyrites; the average copper content is 2 per cent. The daily production of the copper smelters is about 7,500 tons blister copper. This material is shipped to New York and refined to electrolytic copper. The plant consists of seven blast furnaces and four converters together with an agglomeration system of 3 Dwight-Lloyd apparatus. There is obtained from the blast furnace, after the smelting of the pyrites, a pig with a 15 per cent copper content; this is then reworked by the same process to a pig with 30 to 40 per cent copper which is finally converted to blister copper in the basic cylindrical converters. It has been shown that this conversion of the ore to copper in two operations is much to be preferred (for the Bessemer process) to the direct concentration of the copper to 30 to 40 per cent in one smelting period, since, in the first instance, the loss of copper is smaller than in the second case. Nozzles 1.2 in. long and 0.4 in. wide are used in the blast-furnaces and these should stand up well. The blast is not brought to each furnace by means of a separate blower but the blast from all the blowers is brought to a collecting tank and distributed to all the furnaces from this point so that the operation of any given oven is not interrupted by an accident to any one blower. The utilization of the blast furnace gases for the manufacture of sulfuric acid demands that an ore be used which is as free as possible from fine particles; otherwise the resulting gases have too great a flue-dust content. In a suitable apparatus, the fine ore is separated from the coarser particles and the former is agglomerated in a Dwight-Lloyd apparatus. This separation of the fine ore has become very advantageous for blast furnace operation. By this means, a decrease in the coke-consumption has been established and this represents not only a saving in the cost of the combustible but also a better oxidation of the sulfur in the furnace itself, so that there is a higher sulfuric acid content in the gases. A considerable coke-saving has also been obtained by the establishment of a storage system which makes a uniform feeding of the blast furnace possible so that the carbonic acid content of the furnace gases has decreased from 5 to 4 per cent. The smelting process for the conversion of ores, which yield a slag with 28 per cent silicic acid and 45 per cent iron, takes place just as uniformly as the conversion of the pig obtained, to a pig with a high copper content. From the blast furnace for the concentration process the pig is brought in ladles to the basic converters which lie in front of the furnaces and have given good results at this place. The converters, which have an average capacity of 20 tons, are lined with magnesia. The silicic acid required for slagging the ores is added, in several operations, in the form of quartz ores. The flue-dust recovered in the various flue-dust chambers is sintered, with the fine ore, in the Dwight-Lloyd system. This has a capacity up to 100 tons, and on the average handles 60 tons. The cost, per ton, of blister copper was given at \$250, mining cost \$98.25, blast furnace smelting \$97.75, operation of converters \$10.20, freight charges, ore to smelter, pig to the East \$31.60 and overhead charges \$12.20.

**THE DUCKTOWN SULFUR, COPPER AND IRON CO.** has finally succeeded in producing sulfuric acid in lead chambers from the gases from blast furnaces used in smelting pyrites. Part of



their smelter is still in course of construction. The Isabella Smelter now converts about 150,000 tons of ore. When founded in 1899 the company, as its name implies, intended to prepare sulfur from its ores; after much experimentation it has finally succeeded. It now has a sulfuric acid factory with a capacity of about 50,000 tons 60 per cent per day. From the blast furnaces the gases pass through canals to the flue-dust chambers and from there into a cylindrical tower in which they rise to the top in order to pass into another system of flue-dust canals situated at a higher level. This system of canals is of great importance as it serves to regulate the temperature of the gases before they reach the Glover towers and come in contact with the zinc and other vapors. From the flue-dust chambers there is a canal which branches off into the Glover towers. The salt-peter pots are built in this branch. The purified gases, which have acquired a uniform temperature, enter the Glover towers at the bottom, rise through these and then pass out again at the bottom by means of a descending conduit, then enter a special tower and from this reach the lead chambers by means of two large canals. Between the Glover towers, the chambers and the Gay-Lussac towers are placed four large ventilators which serve to drive the gas through the system. These ventilators are arranged in two groups of two each. One group drives the gases into the first chamber while the other group sucks them out from the last chambers. From the chambers the gases pass into the Gay-Lussac towers. The ore converted has a sulfur content of 14 to 19 per cent, average 16 per cent. The plant has two blast furnaces with 21 nozzles along each length. The slag which can be removed is granulated by means of water and is emptied on the slag-heaps. The pigs which are obtained have a 10 per cent copper content and are then concentrated to 50 per cent on blast furnaces by being melted up with pyrites, the material so obtained being sold.

#### CANTON

THE CHAMPION COATED PAPER CO. PLANT is located here and to this fact the town owes its rapid development in the course of four years. The cellulose factory is the largest in the South and, since it is the chief point of interest in Canton, we visited it. Over 1000 workmen are employed in the factory proper while in addition it affords work for several hundred more in the forests which supply the raw material. The plant itself represents a capital of about 3 million dollars. Redwoods, hemlocks, firs and other pine trees are converted by the sulfite process to long-fiber paper pulp while other kinds of trees such as chestnut, poplars, etc. are converted by the soda process to short-fiber pulp. It is estimated that 1000-2000 carloads go through this factory. The power consumption of the plant is 7000 horse-power steam and 8000 horse-power electric power. Both in organization and in kinds of appliances, the plant was especially interesting. In addition to wood pulp, both tannic acid and turpentine are produced in this factory. The tannin is recovered both from the wood and the bark of the chestnuts, 7 per cent being yielded by the former and 10 to 12 per cent by the latter (calculated on dry material). The crushed material is extracted with hot water; after decantation of the solution the residue is rewashed with water and this water is then used as the extracting medium for the next charge. The washes are evaporated to 22-25 per cent while the residues are used as heating material for the boilers.

The sulfurous acid required for the cellulose sulfite is obtained from sulfur in revolving hearth furnaces and is absorbed in lime water. The crushed wood is treated with the sulfite bath in large iron boilers lined with cement and a layer of some resistant material. In the preparation of the soda cellulose, caustic soda (12° B.) is used for dissolving the lignin from the wood-fiber. The dark colored wash from the preparation of the soda cellulose is often revived by being evaporated in a vacuum system, then calcined in a reverberatory furnace to

destroy organic decomposition products; the block soda thus obtained is then washed, the resulting solution being treated with lime and when necessary filtered; the caustic soda thus recovered is used again in the manufacture of cellulose. The vapors resulting in the process of boiling the wood in the caustic are used for the preparation of turpentine.

The wood boiled in the caustic is rewashed by streams of solutions of varying concentrations. The woody-fiber is then put through cylindrical paper mills (which separate the sand from the heavier material) and is then sieved, by which operation the small twigs are removed. It is now bleached in a 3° B. chloride of lime solution, after which the material receives a very careful final washing; the brew, thus obtained, is brought on to a wire frame (in the form of a mill-board) and dried by means of heated rollers. This material is rewashed in the appropriate factories of this company which are situated in the state of Ohio. The production was given as 45 to 44 per cent. Wood-fiber for chestnut wood, 55 per cent for poplar wood and 45 to 50 per cent for pine wood.

#### ASHEVILLE

The district lying around Asheville (which was shown us in a carriage ride given under the auspices of the local committee) is exceedingly beautiful. Asheville lies between two mountains—Black Mountain and Balsom Mountain—which are situated in western North Carolina. From a climatic standpoint it has a wonderful location and it is both the American winter resort of the North and the summer resort of the South. The magnificent summer home of the Biltmore Vanderbilts (with its beautiful park and gorgeous foliage) situated only a few miles from the city, is easily the most interesting place in this neighborhood. The park covers an area of about 152 square miles. The house, English in style, stands in the midst of lakes and transplanted flowers whose magnificent color and blossoms can be developed only in the wonderful climate in which southern plants grow and flourish. It must be pleasant indeed to wander through this park in the beautiful month of June when rhododendrons and various other multi-colored flowers and shrubs are in bloom.

Inasmuch as Asheville was to be the last long stop on the trip, all the excursionists united, at this place, in tendering a farewell banquet to the leader of our little expedition, Dr. D. T. Day, who was to leave us at Washington. This banquet took place in the Park Hotel, whose service in spite of its wonderful situation, is very poor and in which cleanliness appears to be but an unwelcome guest. The requisite amount of liquid refreshment for this affair had to be brought in secretly in suit cases from a beer smuggling station by a committee appointed for the purpose because, according to local laws, the consumption of beer, at least publicly, is not allowed as in other states. Geheim Rat. Knorr, of Jena, made an eloquent address in which he felicitated the leader of our excursion and the valuable services which he had tendered us, while those German ladies who had taken part in the trip showered our honored guest with flowers and presented him with a souvenir as a token of their appreciation and gratitude. Dr. Day proposed the preparation of an album which should contain the best of the amateur photographs taken by the excursionists during the trip. This album was later prepared by a committee in Germany and contained 169 pictures, while several hundred more pictures (which represented only a portion of the photographs) were submitted inasmuch as not all the participants in the excursion were in a position to work up their pictures in the requisite short time. These were placed at the disposal of the excursionists at a nominal price. This collection of photographs will always be a beautiful souvenir of a most interesting trip.

#### CHARLOTTE, NORTH CAROLINA

Saturday, Oct. 19, 1912, was the last day of the excursion

proper, and was spent in an inspection tour, while on Sunday we made the home stretch from Charlotte, through Washington, to New York. A short stop-over was made at Charlotte so that we could study the process of manufacturing cotton and the preparation and refining of cottonseed oil. This little city is the cotton manufacturing center of the South. Within a radius of 100 miles there are 360 cotton factories which operate over seven million spindles and represent a capital of over 150 million dollars. These plants use the water power of the Catawba river.

THE SOUTHERN COTTON OIL CO.—Personally, I joined the party which was to visit the Southern Cotton Oil Co. which recovers and refines cottonseed oil. The cottonseed or cotton oil, which is recovered from the cotton seeds, is an exceptionally important product for the United States. About 600,000 tons of oil (of a value of about 60 odd million dollars) are recovered from over  $3\frac{1}{2}$  million tons of cotton. Cotton seeds are separated from the cotton residues, in which they are lodged, in cotton-gins, which consist of rollers with sharp spikes. The cotton residues go into the proper machines where they are separated into the various grades of cotton; the material thus obtained is bleached by being heated, by steam, with water and bleaching lime, to a temperature of  $110^{\circ}\text{C}$ . and is then treated with acid, washed with water, and finally air-dried. This material is used in the manufacture of mattresses and for similar purposes. The seeds enter the shelling machines, rotating cylinders with sharp knife-blades, where they are shelled. The hulls, after being separated by sieving, are used as fertilizers or mixed in fodders. The kernels are finally ground in a mill and the resulting meal comes into a heated iron container, with false bottom, and agitator, from which it is emptied automatically into a folded cloth on a pre-pressing table. The cloth is folded and the material receives a preliminary pressing. The cake obtained then goes to the press proper, which has 12 tanks placed above one another, and here the oil is squeezed out with a pressure of 300 atmospheres. As so often happens with so many materials, no repressing takes place in this instance. The material is ground and the meal sold. The latter contains 6 to 7 per cent water, 7 per cent oil and 7 per cent ammonia—the nitrogen content is always expressed in terms of this compound. The oil is allowed to settle and is then refined. With a good harvest and dry weather, the crude oil contains less than 1 per cent of free acid; with poor weather its content rises up to 4 per cent and more. The warmed, reddish colored oil is mixed with the calculated amount of  $12^{\circ}$  to  $14^{\circ}\text{B}$ . soda lye, agitated for 15 minutes with a slight increase in temperature, and is then allowed to settle. The oil is decanted, bleached with Fuller's earth and forced through filter presses. Crude oil is worth about 10 to  $12\frac{1}{2}$  cents per qt.; refined oil,  $12\frac{1}{2}$  to 15 cents per qt. The above plant obtains from cotton blossom, 3.5 per cent cotton, 35 per cent hulls, 2.5 per cent sand and dirt, which is a total of 41 per cent, and 59 per cent seed-cake which yields 19 per cent of oil (sp. gr. 0.92), calculated on the seed at pressing.

#### GREAT FALLS AND NITROLEE

SOUTHERN POWER CO.—We made a little trip from Charlotte to Great Falls and Nitrolee to see the power plant of the Southern Power Co., at Great Falls, and the factory for the conversion of atmospheric nitrogen to nitric acid by the Pauling process. This last visit was easily the most interesting of our entire tour. We were received most cordially by Engineer Pauling from Cologne on the Rhine (who was there in order to set the plant in operation) and his two assistant engineers; after an introductory lecture by Pauling, we were shown through this highly interesting establishment. The power house of the Southern Power Co., situated at Great Falls, utilizes the fall of the small but turbulent Catawba River for the production of electricity. In the course of 5 miles the river has a drop of about 137 feet. This drop is utilized in 2 falls (one of which is 72 feet and the other 65 feet) made by 2 dams. At each dam, 30,000 horse-

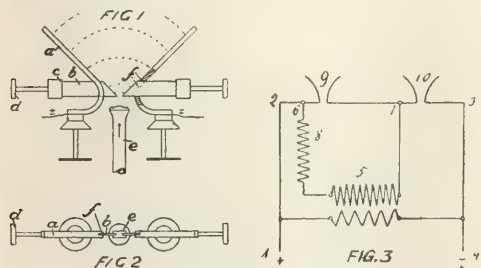
power of electric energy are produced while at another plant, situated further up the river, 24,000 horse-power more are gained. In the main, the electrical energy is used in the cotton industry of the neighborhood. The amount of water at Great Falls (being, naturally, dependent on the time of the year) varies between 3,000 and 175,000 cu. ft. per second. The generators for the electric current are directly coupled to horizontal turbines and produce current at an E. M. F. of 2,500 volts. A set of 16 transformers transform the current into one of 50,000 volts, while another transformer system then changes this to 100,000 volts. At about this E. M. F. it is sent to the distributing stations in Charlotte. The electricity is sold at two prices. The lower price is for those consumers who do not require a guaranty of a specified current, but who can, however, use to advantage any excess current available, e. g., the nitrogen recovery plant at Nitrolee—while the higher price is for those consumers who demand a guaranty of a given total amount of power per month.

The process of the Saltpetersäure-Industrie-Gesellschaft, G. m. b. H., in Gelsenkirchen (founded by the brothers, H. and G. Pauling) was first tested and worked out in Patsch, near Innsbruck. The plant at Innsbruck now employs about 15,000 horse-power (in 24 furnaces) and has a daily production of 10,000 kg. of 98 per cent nitric acid. The Pauling process for the recovery of nitrogen from the air is better than the process of Eyde and Schoenherr, which, in operation, requires a constant E. M. F., because the operation of the furnace suits the E. M. F. at any given time. The most important patents on which the Pauling process for the preparation of a highly concentrated nitric acid from atmospheric nitrogen is based are German Patents 193,366, 198,241, 205,018, 213,710, 244,840, 246,712, and 257,809.<sup>1</sup> Flaming arcs which have been produced between electrodes bent in the form of crescent-shaped lightning rods are used in the process. The flaming arc, which is situated at the narrowest point between the two electrodes, broadens out following the forcing of the hot gases to the top and breaks after each half period of the alternating current, to form anew at the narrowest point between the two electrodes. A current of air blown between these electrodes broadens the arcs still more so that flaming arcs of considerable length develop. Since the air forced in rushes through so very rapidly, a very high E. M. F. (for the relatively small space between the electrodes) is required for the ignition of the arc but, naturally, this sinks considerably, at the moment of arc formation. The Pauling ignition arrangement can be used for the formation of a high-tension flaming arc in which as large as possible an amount of energy is discharged by the aid of a rapidly moving gas stream, and which consists of two movable ignition electrodes (in the form of knife blades) which neither disturb nor retard the gas stream in any way. These narrow ignition-blades are placed by hand opposite one another in the space (only a few mm. in size) between the two electrodes which serves for the uniform burning of the arc. The flame burns very quietly with a blinding white light 1 meter long. The water-cooled electrodes are of iron. Every two arcs burn within a brickwork furnace. To effect the disposition of several flaming arcs in a series in one and the same current circuit, the Saltpetersäure-Industrie-Gesellschaft uses their arrangement which is protected by German Patent 213,710. In the operation of the high tension electric arcs, which serve for action on gases, the resistance of the air spaces is exceptionally high, but this resistance sinks to quite a small quantity at the moment that the spark pierces the space. Accordingly, an increased resistance (which corresponds to the current strength of the discharge) must be inserted in the circuit so that the difference in E. M. F. before and after the spark is destroyed. Because of the difficulties which the process presents, the inventors decided to give the working current circuit an E. M. F. which

<sup>1</sup> Chem. Zelt. Repert, 1908, pp. 108, 178, 277; 1909, pp. 7, 531; 1912, pp. 234, 302; 1913, p. 166.



approximates the normal working E. M. F. of the arc, while that required for sparking is obtained by the use of a relay (or auxiliary) current of considerably higher E. M. F. but smaller power. In addition, one pole of the auxiliary circuit is connected with an outside pole of the working current while the other pole is connected with the inner pole of the arc-current circuit. In this way, the auxiliary circuit is prevented from discharging through the working circuit; furthermore, the arc space which bridges over the auxiliary circuit must be ignited by the high tension circuit. All the arcs, arranged in series in the high tension circuit, must, therefore, be bridged, in each case by a special high tension circuit, and the latter (which is an auxiliary high tension circuit) has a much higher tension than the main high tension circuit. The arrangement, as used by the inventors, is as follows: The auxiliary circuit (6, 7) is started directly from the working current circuit (1, 2, 3, 4) by interposing a suitable



transformer which "steps up" to a sufficient degree the E. M. F. of the current taken from the working circuit before the latter enters the bridged portion of the working arc space. The above arrangement permits the operation of any number of ovens desired in one and the same circuit without the arc from any one having any untoward influence upon any other. This, also, permits the efficient utilization of all the energy available at any time. The electrical ovens work at 5000-7000 volts. When in full swing, the current strength in the oven is about 270 amperes. Two arcs are placed in series. To start an oven, an arc transformer changes the E. M. F. in the oven to 16,000 volts. The gases evolved in the oven are divided, one portion going to the blast-heater and the other portion giving up its heat to a steam boiler. Thus the temperature of the gases is lowered from 1200° C. (the temperature at which they leave the oven) to 200° C. The gases then heat an acid concentrating tower and are finally chilled in a cooler to 30° C. From this point the gases pass through 4 absorption towers, being washed in one of these in a stream of calcium hydroxide and in the other three in a current of water. The final gases are then led through two towers which are irrigated by 80 per cent sulfuric acid.

The 40 per cent HNO<sub>3</sub> which is recovered from the towers is treated with 94 per cent sulfuric acid (in the proportion of one part nitric acid to two parts sulfuric acid) in a tower through which steam passes from the bottom up. Ninety-eight per cent nitric acid passes off from the upper end of the tower while sulfuric acid, diluted to 68 per cent, flows out below; this sulfuric acid is re-concentrated for further use in the above-mentioned sulfuric acid concentration system which is heated by the hot gases. Complete denitration takes place in the tower simultaneously with the concentration of the nitric acid. Four-fifths of the nitric acid produced are obtained from the washing of the gases in water and the remaining one-fifth is recovered in the tower washed by sulfuric acid. In connection with the plant for the recovery of nitric acid, there is also a plant for the production of sodium nitrate. The yield is 60 g. nitric acid per kilowatt-hour.

NEW YORK, TORONTO, COBALT, BOSTON

That night our special train took us back to Charlotte and we

reached New York after a 17 hour ride *via* Washington. We made a stop-over of several minutes in Washington, where our worthy guide, Dr. Day, left us. The trip to New York, which was quite familiar to all of us because of the ride to the opening of the congress, passed only too rapidly and during it we were busily occupied in active preparations for leaving our traveling hotel and in leave-taking from all those acquaintances with whom we had lived and experienced so much for the 35 days from Sept. 16 to Oct. 20, 1912. Arrived in New York, the company of excursionists quickly disbanded; the majority sailed for home the next day by various steamers and but few remained to supplement their knowledge of the American aspect of their various specialties by trips of their own. I was detained by the desire to become acquainted with the mines of the Cobalt district in the state of Ontario, Canada, and to visit my colleague, H. O. Hofman, and become acquainted with the methods of procedure in his interesting school, the leading metallurgical institute of the United States, which is under his direction. Before I started north I visited a few smelters in the vicinity of New York.

Once more my path led to Niagara Falls. How differently did it appear this time! Rain and cloudy weather did not accord the Falls the same magnificent appearance they had presented when viewed in brightest sunshine as when we visited them in September. The foliage had turned sear and yellow, had fallen from the trees, and the friendly intercourse between visitors had entirely disappeared, so that the spot held no attractions for a prolonged stay. Toronto, which I saw under a driving rain, also kept me but a few hours; these I utilized for an external inspection of the University buildings and a visit to a collection of historical paintings, etc. (relating to Canadian history), in the University Library Building. After that I remained two days in Cobalt, where I was most delightfully entertained by Mr. Gordon, the manager of the Cobalt Lake Co. Finally, before my return home, I spent two days in Boston with Prof. H. O. Hofman, at whose hands I received a most cordial reception. Under his guidance, I visited the interesting and famous buildings of the Massachusetts Institute of Technology. An entire day was spent in visiting the Departments of Metal Smelting, Metallurgical Laboratories and Ore-dressing. An extremely interesting event takes place on Tuesday of each week. All the various apparatus, machinery, etc., is put into operation and groups of students are assigned to these so that the theoretical discussions with which they are favored in the various lectures are in this way supplemented by practical demonstrations. On a wonderful moonlight night one of those splendid coast steamers brought me from Boston to New York, landing me at the latter place on the morning of Oct. 30, 1912.

#### THE RETURN TO GERMANY

After the disposal of a few final business matters, I left the shores of America on the next day—Thursday, Oct. 31, 1912—on board the Lloyd steamer "George Washington," which carried back with it the last of those who had participated in our magnificent tour of the continent. During the rather quiet sail we recovered in a most pleasant way from the extreme exertion of sight-seeing. Our arrival at Bremen was delayed by the foggy weather we encountered in the North Sea, but with much joy we stepped ashore early on Saturday, Nov. 9th. The remaining few excursionists made their last parting adieus in Hanover, as from this point on their paths lay in different directions.

After a three months absence from home and Germany, we once more resumed the accustomed routine of our daily lives. It is with a feeling of pleasure that I, as well as every other person who participated in this splendid tour through an intensely interesting country, look back upon the life and stress of which, in several weeks, we could catch but a glimpse. Even though we have returned with much joy to our homes and our usual activities after the conclusion of this tour, each of the excursionists will cherish the wish to be able to re-visit, in the near future, that land of unbounded potentialities.



# AMERICAN INSTITUTE OF CHEMICAL ENGINEERS

The Sixth Annual Meeting of the American Institute of Chemical Engineers was held in New York, with headquarters at The Chemists' Club, December 10 to 13, 1913.

The Council met on Tuesday evening, December 9th, for the transaction of routine business with President Wagner in the chair. At the first business meeting on Wednesday, the following officers were elected for the ensuing year:

*President:* M. C. WHITAKER, Professor of Chemical Engineering, Columbia University, New York.

*First Vice-President:* RICHARD K. MEADE, General Manager, Tidewater Portland Cement Company, Baltimore.

*Second Vice-President:* G. W. THOMPSON, Chief Chemist, National Lead Company, Brooklyn.

*Third Vice-President:* A. C. LANGMUIR, Superintendent of Factory, Marx & Rawolle, Brooklyn.

*Secretary:* J. C. OLSEN, Polytechnic Institute, Brooklyn, New York.

*Treasurer:* F. W. FRERICHS, Manufacturing Chemist, St. Louis.

*Auditor:* H. M. KAUFMANN, General Manager, Mutual Chemical Company of America, New York City.

*New Directors:* HENRY HOWARD, Vice-President Merrimac Chemical Co., Brookline, Mass.; JOHN C. HEBDEN, Vice-President and General Manager, Franklin Process Co., Providence; I. P. LIHME, Engineer, Grasselli Chemical Co., Cleveland, Ohio.

The local arrangements were in the hands of President Wagner and Secretary Olsen. In addition to the regular program, the members of the Institute visited a number of the large industrial plants in and about New York City, the more important of which were as follows: The Barber Asphalt Paving Co., Maurer, N. J., under the personal guidance of Dr. Clifford Richardson; the Sanitary Utilization Company at Barren Island, under the guidance of Dr. Maximilian Toch; The Willard Park Hospital and Laboratories of the New York City Department of Health, under the guidance of Dr. Ernest J. Lederle, Commission of Health; the plant of Hanson & Van Winkle Company, electroplatin, Newark, N. J., and the Atha Works of the Crucible Steel Company of America, under the guidance of Dr. George W. Sargent; and the Chemical Engineering Museum and Laboratories of Columbia University.

The members also attended, by special invitation, the International Exposition of Safety and Sanitation which was in session at the Grand Central Palace.

For the final meeting, the Chemical Engineers participated in a joint meeting of the American Chemical Society, Society of Chemical Industry and American Electrochemical Society which was a symposium for illustration of the various forms of welfare work obtaining in some of the more important chemical industries.

The Annual Dinner of the Institute was held in the dining room of The Chemists' Club on Thursday evening, President Wagner acting as toastmaster. The INSTITUTE MEDAL was presented to Dr. F. W. FRERICHS, for his valuable contributions to the Proceedings of the Institute on "Some Problems in Chemical Engineering." The presentation address was made by President Wagner who emphasized the importance of the papers presented by Dr. Frerichs, especially from the standpoint of their educational value to students. Exceedingly interesting and amusing after-dinner speeches were made by Mr. Arthur Von Briesen, the distinguished patent attorney, who spoke on "The Relations of the Chemical Engineer to the Patent Laws;" Dr. Chas. F. McKenna, recently elected President of The Chemists' Club, who spoke on "The Chemists' Club and its Relation to the Institute;" and by Prof. Chas. F. Chandler whose subject was "The Chemical Industries of Sixty Years Ago."

## PAPERS

**The Effect of Legislation on Chemical Industries.** Presidential Address by DR. T. B. WAGNER.—This Address was a systematic treatment of this great industrial problem and is published in full in this issue of THIS JOURNAL.

**Sanitary Control of the City of New York.** By DR. ERNEST J. LEDERLE, Commissioner of Health, City of New York.—This address was a comprehensive outline of the organization and equipment provided for handling the sanitary problems of Greater New York. The speaker gave an interesting description illustrated by lantern slides of the clean-up campaigns which had been conducted under his administration, and also illustrated and described the various provisions in the city for handling contagious and infectious diseases. This talk formed the basis for the visit which the members paid to the laboratories and hospitals of the Department of Health.

**Recent Developments in Commercial Explosives; and Electrolysis Using Supported Mercury Kathode.** By E. A. LESUEUR.—These proved to be very interesting papers and will be published in full in a later issue of THIS JOURNAL.

**A New Form of Self-Dumping Filter Press.** By E. J. SWEETLAND.—After a general discussion of the theories and problems involved in the separation of large quantities of solid from liquid, Mr. Sweetland exhibited a working model of his press and demonstrated its operation. He later showed a large number of lantern slides illustrating installations in successful operation as applied to a wide variety of industrial processes.

**A New Principle in Filter Press.** By DR. ALFRED BURGER.—The speaker discussed in detail the results of his investigations on the filtration and washing of precipitates. These investigations have led him to the conclusion that the present system of forcing the wash water through the cake regardless of the direction of the flow of the filtrate is a practice which is not only responsible for the loss of large amounts of time, but also results in a low washing efficiency. As a result of his conclusions, he has re-equipped a number of standard filter presses with frames so arranged that the wash water can be made to follow the direction of the filtrate and this without interruption of the flow. The results obtained on large scale installations justify him in claiming that he can reduce the time required for filtration and washing of slimy precipitates from twelve hours to two hours, and in other cases from six hours to one hour. Dr. Burger's paper was discussed by the members with great interest.

**Ozone; Its Manufacture and Use.** By DR. A. VOSMAER.—The subject of ozone was discussed under the headings of Formation, Chemistry and Application. The author has definitely determined the character of spark and the efficiency factors requisite to the production of ozone. The paper was illustrated by a number of lantern slides describing the generating apparatus and also the existing installations of water sterilizing equipment. The fundamental principle that the efficiency of the sterilizing treatment is a function of concentration and time was emphasized, and the discussion brought out the various relations between time, cost and efficiency of water purification.

**The Present Status of the Wood Turpentine Industry.** By E. H. FRENCH and JAS. R. WITHROW.—The paper was presented by Professor Withrow and after a brief outline of the various well known processes for recovering wood turpentine, the industry was carefully analyzed, first from the standpoint of the engineering problems and requirements, and later from the commercial standpoint. A number of the members who are directly engaged in the manufacture and sale of turpentine contributed interesting and important material to the discussion.

**Symposium on Comfort, Welfare and Safety Provisions in Chemical Works.**—MISS FLORENCE HUGHES who has charge of

the welfare work of the New Jersey Zinc Company's plants presented an interesting paper illustrated by a large number of lantern slides on the welfare work under her direction. This was followed by a paper by MR. HOWARD LYON, Physicist for the Welsbach Company, on welfare work and the safety provisions in operation in the Welsbach Company's plants in Gloucester, N. J., and Columbus, Ohio. This paper was also illustrated by lantern slides. The safety provisions for the National Lead Company were discussed and illustrated by MR. C. P. TOLMAN, and the program was concluded by an address by DR. FRANCIS D. PATTERSON, of Harrison Bros. & Co., of Philadelphia. Dr. Patterson illustrated his talk by numerous lantern slides and two moving picture films, one demonstrating the workman's risk as a result of the disregard of safety devices on moving machinery, and another illustrating the work of the United States Steel Corporation at Duquesne, Pa., in the training and development of the children of their employees.

**Committee Reports.**—Two important committee reports were submitted at this meeting and will later be published in full in THIS JOURNAL.

PROF. J. R. WITHROW, Chairman of the Committee on Education of Chemical Engineers, submitted a report outlining the progress of the work during the past year and offered for discussion and approval of the Institute important suggestions for future work.

The Committee on Standard Catalogue for Chemical Engineering Equipment, represented by DR. WM. M. GROSVENOR, outlined a plan for the work which this committee proposes to undertake. This plan received the hearty approval of the Institute, and no doubt the work of this committee, under the guidance of Dr. Grosvenor, will result in the much to be desired standardization of a chemical equipment catalogue.

## THE EFFECT OF LEGISLATION UPON CHEMICAL INDUSTRIES

### PRESIDENTIAL ADDRESS

By T. B. WAGNER

At the end of the eighteenth century an observation was made by Scheele in his laboratory, the results of which have meant more to the prosperity of all peoples inhabiting this planet than any other invention—chemical or otherwise. I am referring to the observation which disclosed the fact that cyanide of potassium is capable of dissolving gold. While this discovery was of much scientific interest at the time, and led Faraday to explain it by an elaborate theory, no industrial application was made of it until about one hundred years later. In April, 1890, the first plant operating under the McArthur-Forrest method for treating ore tailings was started in Johannesburg. The effect of this process is reflected in a tremendous increase of the world's output of gold; consequently, the cyanide process plays an important part in the monetary system of the world, as the increased gold production effected by it has dispelled the fear that there might not be enough of the precious metal to maintain the gold standard of the civilized nations. The struggle in this country for the maintenance of the gold standard is within the memory of all, but I fear that, as in other instances, credit was not given to the chemist for his share in having the gold standard preserved.

The recital of this invention has no immediate bearing upon my subject; except in so far as it goes to prove that the furtherance of civilization and the furtherance of industries depend largely upon underlying conditions, which, in their incipency, may seem trivial. That is the case with the effect of legislation upon the development of chemical industries. The chemical industries of the world are a little over one hundred years old, yet, in point of advancement and financial returns, their success is without a rival. Strange as it may seem, the starting

of industrial enterprises is not always due to the chase for the almighty dollar, as is generally and perhaps pardonably assumed, but in many instances it is directly caused by the enactment of laws with more or less restrictive tendencies.

### THE BEET SUGAR INDUSTRY

Let us go back to the birth of the chemical industries in the beginning of the last century. Napoleon the First, whose fame as a statesman and as a conqueror will stand like a beacon light as long as history shall be written, was at war with England. To crush his rival, this far-sighted statesman conceived the idea that the most effective way of accomplishing his purpose lay in the crippling of England's trade. The Continent naturally was the principal buyer of England's colonial products. Napoleon, therefore, in 1806, issued a *ukase*, according to which England's colonial products were barred from the Continent, and all trade relations with England were forbidden; any country violating this *ukase* was apt to find itself involved in war with France. This *ukase* is known as Napoleon's "colonial blockade." Among England's most important colonial products was cane sugar, but with the enforcement of the blockade, the Continent found itself unable to obtain this sweetening agent, without which life seems to be less sweet indeed. The price of sugar rose enormously and an impetus was thus given to the exploitation of the discovery of Margraf, made in 1747, that the ordinary garden beet root contained considerable quantities of sugar, identical with that found in the sugar cane. The first factory was built in Germany in 1801. Since then, this industry has had a marvelous growth, and the present production of sugar from this source exceeds that from cane. The world's production of sugar to-day is 18,500,000 tons, of which 9,000,000 tons are obtained from the sugar cane, and 9,500,000 from the sugar beet. Of the latter only a little over 600,000 tons are produced in this country, the factories engaged in its manufacture numbering 72. Incidentally I might mention that while at the beginning of the industry about twenty tons of beets were required for the production of one ton of sugar, the same amount of sugar is now obtained from only seven tons of beets. It is also worthy of mention that all of the potassium contained in the sugar beets and fully 65 per cent of their contents of nitrogen are recovered from the molasses and utilized over again. What effect the latest legislation, the new tariff, will have upon the industry in this country, whether it will prove that it has outgrown the state of an infant industry, or whether it still requires the friendly and substantial support of a high protective tariff—that the future will demonstrate within a few years.

### THE PRODUCTION OF GRAPE SUGAR FROM STARCH

Coincident with the establishment of the beet sugar industry was that of another industry which was destined to play an important part in the economic conditions of this country and Germany, *viz.*, the production of grape sugar from starch. The success of this new industry, it may be rightly assumed, is also attributable to Napoleon's exclusion of England's cane sugar from the Continent. The conversion of starch into a reducing sugar, by means of a dilute acid and heat, was discovered in 1811 by Kirchhoff, a teacher at the Imperial Academy of Sciences at St. Petersburg, and the first factory was built in Germany in the same year by the Grand Duke of Saxe-Weimar, at the instance of Professor Doebereiner, of the University of Jena, whom you will remember as the inventor of the first "hydrogen lamp." Bearing in mind the present magnitude of this industry, it is interesting to read of the financing of this pioneer factory in Germany. I quote from a letter of the Grand Duke to Professor Doebereiner:

"The subscription is assured; my wife and I, my son and his wife are the four stockholders, each contributing one hundred taler. I shall advance the capital of four hundred taler, which is to bear interest at five percent, and shall turn this over to you;



you may then proceed immediately to start the plant. I shall deed my shares to you; I wish you every success and I am convinced that you will proceed carefully. As regards the concession I believe it can be arranged that it shall be granted for a period of years; however, it must not include the home production of syrup for home use. I intend coming to Jena this week; I shall then bring the money with me and we may discuss further details. I have looked up the manufacture of sulfuric acid in Chaptal & Klaproth. It seems to require a large capital, however, to build the lead chamber."

From this small beginning, the industry has grown into one of vast proportions, the yearly production in Germany being 120,000,000 pounds, and whereas, at the start, only grape sugar and syrup were produced, and the potato was the only form of raw material, at present by far the largest amount is produced from Indian corn and the number of different commercial commodities produced from the latter reaches almost one hundred. The industry consumes, in this country, about fifty million bushels of corn annually, or practically one-sixth of all the corn which reaches the markets. These figures must not be interpreted as meaning a steady and unhampered growth of the industry. On the contrary, if all the legislation enacted had had the effect anticipated at the time of enactment, the industry would not have survived these attacks. For instance, in various states, laws were passed putting glucose and grape sugar in the same category as poisons and prohibiting their use in food products. Only last year, attempts were made in the legislatures of two states to exclude glucose from use in confectionery, although it is conceded that its use results in a better grade of candy and that certain goods cannot be made without it.

#### THE WINE INDUSTRY

Again, when it was discovered by Dr. Ludwig Gall that grape sugar lends itself admirably to the improving of wines, in which the amount of sugar produced by nature is deficient on account of adverse climatic conditions, this method of ameliorating wines, which has come to be known as "Gallizing," was hailed in Germany as one of the most important discoveries, affecting and improving the economic conditions of the provinces in which the wines were produced. Owing to the large demand which Dr. Gall's discovery created for this sugar, it contributed materially to the growth of the industry. Yet we find that only a few years ago conditions were reversed by legislative action and great restrictions were placed upon the use of this sugar in the amelioration of wines. In this country, the controversy over the use of sugar in wines, only a few months ago, almost caused the failure of the new tariff act. Our domestic wine industry is centered principally in the State of California on one side, and the States of Ohio and Missouri on the other. California produces grapes rich in sugar, whereas, even the best grapes produced in Ohio are deficient in sugar to such an extent as to produce a wine so low in alcohol as to be almost unmerchable. The Ohio and Missouri wine producers, therefore, resorted to "Gallizing" ever since the industry was started in their states, about 60 years ago. Their ameliorated wines are said to be as good as any produced in California, yet the wine producers of that State tried to create the impression in Congress and elsewhere that California wines were the only pure wines, whereas, those produced in Ohio and Missouri were adulterated because of the addition of sugar. In the production of sweet wines it becomes necessary to "fortify" the wines with brandy, and the California people succeeded in having an act passed by Congress in 1890, which permitted them to use brandy without paying the spirits tax of \$1.10. It is said that since the passage of this act, the amount of money saved to the California interests was not less than \$63,000,000. To retaliate against California, the Ohio and Missouri interests appeared before Congress when the Underwood tariff bill was under consideration. One section of the tariff act deals with the income derived from

internal revenue, and here the Eastern interests saw their opportunity and introduced a bill which would take from the California wine producers the privilege of using tax-free brandy. It would compel them to pay into the United States Treasury annually something like \$8,000,000. The California interests answered in kind by introducing a bill, placing a tax of twenty-five cents per gallon upon all wines produced in the territory east of the Rocky Mountains, which, if enacted into law, would mean the annihilation of the industry in that territory. This, in turn, would injure the grape sugar industry, as it would curtail the consumption of grape sugar. Further consideration of the tariff bill came to a standstill, as this so-called wine clause proved the stumbling-block, and no headway was made until the entire wine clause was eliminated for the time being—Congress agreeing to give it attention during the regular session.

I cite these cases to show the influence of legislation, even though indirect, upon the development of a chemical industry. What is one's loss is another's gain. For instance: the loss of the sugar business to England meant the birth of two important new industries and these in turn influenced the development of other branches of the chemical industries. It is but fair to state that the chemical industries in general owe a great deal to the beet sugar industry. Looking over the list of early chemists, and chemical engineers, who have distinguished themselves in the chemical industries, we find that most of them had their start in a beet sugar factory, likewise many successful works managers, for it was in this industry that the first complicated machinery was installed. The modern evaporating devices as well as the separation of solids from liquids by centrifugal force had their inception in beet sugar works.

I cannot leave this chapter without mentioning another instance bearing upon the beneficial, although unlooked for, results of restrictive legislation. A number of years ago a law was enacted in one of the wine-producing countries abroad with reference to wines made from the residue of the pressings of the grapes, the so-called "Pomace" wines. These wines were introduced by Pétiot, a French wine merchant, and were produced from Bordeaux wines by adding a sugar solution to the residue from the first must and fermenting a second time. The alcohol generated thereby dissolved coloring substances, as well as tannin and the flavoring principles, the "bouquet." This treatment is known as "Pétiotizing" and is applied to Bordeaux wines four or five times in succession. Much sophistication was practised—the pomace wines being sold frequently as natural wines. That government recognized the legitimacy of the "pomace" wines business, but it wanted these wines to be sold for what they were and did not want them sold to the public under a misleading name. The wines were supposed to be sold as "Pomace Wines," and to enable the government officers to distinguish them from "natural" wines, and to identify a pomace wine, the law provided that these wines must receive, before marketing, the addition of a small amount of phenolphthalein. The Inspector would examine the wines by adding a few drops of an alkaline solution which, of course, would turn the color red. If the color of a "natural" wine turned red, it was *prima facie* evidence that a pomace wine had been substituted. After this law had been in effect for about a year, it was observed that peasants living in the district where these pomace wines were produced, and consuming rather large quantities of these wines, developed what was then considered a disease and which assumed the proportions of an epidemic. The government dispatched its medical officers to make a thorough investigation, and subsequently they reported that they believed phenolphthalein to be the cause of the trouble. Thereupon clinical tests were instituted and the fact established that phenolphthalein was a most effective cathartic. While heretofore phenolphthalein was used primarily in the laboratories as an indicator, it now assumed an important position among our



therapeutic chemicals and is at present manufactured in very large quantities.

#### THE USE OF SACCHARIN IN FOODS

Before leaving the subject of sugars, I must not omit a reference to saccharine, a substance which has received extensive attention at the hand of legislative bodies. As you know, saccharine was discovered by Dr. Fahlberg, while taking a post-graduate course with Prof. Ira Remsen at Johns Hopkins University. It was more or less an accidental discovery, as Dr. Fahlberg's work was in the direction of coal tar derivatives from a purely scientific point of view. The manufacture of this new sweetening agent was started in Germany and a new industry created which grew in importance so that it was eventually considered a menace to the beet sugar industry of the Continent. The latter, of course, is of greater importance to continental countries from an economic point of view, and the new rival of beet sugar was, therefore, discriminated against by laws which prohibited the use of this sweetening substance as a substitute for sugar, permitting its employment solely for medical purposes, the Governments of Germany and Italy going so far as to prohibit the manufacture of the article itself. It was not prohibited because the article was injurious to health, but simply because of economic considerations. The importation into Germany being prohibited, it is interesting to note the accounts in the trade papers of the vast amount of smuggling from Switzerland into Germany. Incidentally this shows that notwithstanding the prohibition of saccharine in food, a large demand for it still exists, and I am told that it is used chiefly in the households for sweetening jellies, jams, preserves and similar products in place of the expensive beet sugar, rather than by the manufacturers of such products. I read an account in one of the trade journals recently, according to which it was observed for some time by the Customs authorities that an astoundingly large number of funeral parties crossed the Swiss frontier into the adjoining Grand Duchy of Baden—the explanation given being that the bodies were shipped into Germany in conformity with the wishes of the deceased to be buried in their native land. The number of funeral parties steadily growing in numbers, the Customs authorities finally had their suspicions aroused and ordered a casket to be opened. It was discovered that in place of the supposed corpse, the casket was filled with packages of saccharine!

#### THE CONTACT PROCESS FOR SULFURIC ACID

The most far-reaching legislation ever enacted was that directed against the discharge of sulfurous acid fumes from ore smelters. With the increased output of these smelters, the volume of sulfurous acid discharged into the air became so large as to produce a most destructive effect upon vegetation. Laws were enacted in this country, as well as abroad, to the effect that unless the sulfurous acid fumes could be rendered harmless, the operation of these smelters would have to be stopped. The first attempts to convert them into a useful article were in the direction of compressing the gases into liquid sulfurous acid, which was used in the manufacture of glue and gelatine, but the amount of gas recovered from the furnaces grew so enormous that this outlet was not sufficient to take care of the supply. The attempts were then directed to oxidizing the sulfurous acid by means of the oxygen of the air for the production of sulfuric trioxide, following the re-action discovered by Clemens Winkler. These efforts proved extremely successful, and works were soon established where  $\text{SO}_2$  and finally sulfuric acid was generated from the waste sulfurous acid gases. In this manner a new process for manufacturing sulfuric acid was created, the so-called "contact process," which, in the course of time, thoroughly revolutionized a branch of chemical industry in which the old established chamber process had come to be considered impossible of improvement.

I am particularly pleased to be able to refer in this connection to the splendid work of our fellow member, Mr. J. B. Francis Herreshoff, whose contact process has proven so superior to that of the Badische Anilin and Sodafabrik in point of economy and simplicity of operation that it is now being introduced into Germany.

The utilization of the waste gases from smelters had the effect of producing cheap sulfuric acid in localities where it would have been impossible to produce it by any other method. This had the most beneficial effect upon the development of the fertilizer industry in this country. Our southern states, principally Florida and Tennessee, furnish to-day the bulk of the world's requirements of phosphatic rock. Liebig showed us how this insoluble phosphorus could be converted into a soluble form by a treatment with sulfuric acid, and for this purpose alone over 3,000,000 tons of acid are used per annum.

The contact process, in turn, was responsible for the successful commercial production of synthetic indigo. The most successful method of producing it is a combination of methods suggested independently of each other, and consists in the following steps:

1. Naphthalene to phthalic acid.
2. Phthalic acid anhydride to phthalic imide.
3. Phthalic imide to anthranilic acid.
4. Anthranilic acid to phenylglycin ortho carbonic acid.
5. Phenylglycin ortho carbonic acid to indigo.

The greatest problem was the production of phthalic acid. Heretofore it had been obtained through the oxidation of naphthalene by chromic acid. The latter, however, was very expensive and this method did not hold out much hope of commercial success. E. Sapper, a chemist engaged in experiments to reduce the cost of production of phthalic acid, conceived a new process of making it by heating naphthalene with highly concentrated fuming sulfuric acid. After years of experimenting, a suitable method was found, in the discovery of which Accident, the patron saint of the inventor, played an important role. It was discovered that the addition of mercury to the solution of naphthalene in fuming sulfuric acid facilitated the re-action and resulted in an almost theoretical yield. We must bear in mind, however, that the commercial success of synthetic indigo was influenced, to a large extent, by the fact that the  $\text{SO}_2$  generated by the process of heating naphthalene with sulfuric acid could be re-converted into  $\text{SO}_3$  by the contact process. Even ten years ago one single establishment engaged in the manufacture of synthetic indigo re-converted into  $\text{SO}_3$  40,000 tons per year of sulfurous acid obtained in the manufacture of phthalic acid.

Thus we have seen that through the instrumentality of the law, a chemical process was introduced into metallurgical establishments, the contact process was created, a cheap supply of sulfuric acid was secured which, in turn, proved a blessing to agricultural interests through the production of a cheap fertilizing material, and finally it made possible the commercial exploitation of one of the finest achievements of scientific effort—the production of synthetic indigo.

#### POLLUTION OF STREAMS

Another impetus was given to chemical industries by laws aimed at stopping the contamination and pollution of rivers and other waters. Before the value of by-products was understood by manufacturers, the rivers and water-ways in general were used as the most convenient and inexpensive way of removing offal and waste of all kinds from the factory. It is not difficult to understand the results from such abuse of natural water courses. The communities deriving their supply of drinking water from these sources were especially affected by it; the water, deprived of its natural content of oxygen, caused the death of the fish inhabiting these waters and the odor produced by the decomposition of this offal brought much dis-

comfort to the people living within the vicinity of such streams. It was a condition of which the Legislatures were compelled to take cognizance, and the inevitable result was the prohibition of such use of the streams. This legislation proved disastrous to many industries but it proved of the greatest benefit to a far larger number. Among others, it affected beneficially all the industries connected with fermentation and those connected with the manufacture of starch from various raw materials. The materials recovered from the waste of these industries were converted into dry form, serving, in most instances, for the feeding of cattle and live stock. Such feeds are those produced from the starch works, distilleries and breweries, and they rank among the most valuable concentrated feeding-stuffs. They are indispensable for the rational feeding of live stock, which, together with wheat, form the principal means of sustenance of mankind. The production in this country of feed-stuffs from the manufacture of starch alone amounts to over 300,000 tons per year, and since these feed-stuffs sell at approximately \$25 per ton, the revenue obtained from this source amounts to \$7,500,000 per annum.

In former years, it was customary to allow the germs of the corn to go to waste, but to-day the industry recovers about 75,000,000 pounds of oil per year, which is sold in the 'markets of the world at about \$4,500,000. The corn solubles—the so-called steep water—are now recovered to the extent of 100,000,000 pounds a year, which are sold also in the world's markets at over \$1,000,000. The by-products recovered from distilleries and breweries in this country may be said to be worth about \$5,000,000 per year.

#### OLEOMARGARINE

One of the most prolific sources of legislation is oleomargarine. Laws have been enacted in many states aimed at the destruction of this industry, as for instance the oleomargarine laws of Pennsylvania and New Hampshire, which required that no oleomargarine should be sold in those states unless it were colored pink. Yet, in spite of these restrictive, if not prohibitive, laws, this industry has prospered, simply because of the underlying merit of the product itself. This is well illustrated by the fact that the receipts of the internal revenue office from the tax on oleomargarine amounted to \$1,259,987.65 during the fiscal year ending June 30, 1913. This subject furnishes a most interesting sidelight on the incongruities of laws. The artificial coloring of natural butter is permitted by a special act of Congress, even though the butter color used at the time of the enactment of this law would not be permitted to-day under the Federal Food & Drugs Act because of its injurious character.

The artificial coloring of oleomargarine, however, is not permitted, because such practise would make it an imitation of butter. If, however, the producer of oleomargarine is willing to pay a tax of 10 cents per pound, he then acquires the right to put his "fraudulent" product upon the market and the government becomes his silent partner. Most of the oleomargarine is produced by the packers, but it is only one of a large number of chemical products manufactured by them. It is only a relatively short time since chemistry has entered the packing houses and it was not entirely a matter of choice that led to the entry of the chemist, but rather stern necessity, for the law had served notice upon the packers that a stop would soon be put to their practice of discharging their enormous putrefactive wastes into creeks and rivers. This could not be accomplished without the aid of the chemist and the chemical engineer. As a result of their work, the packers produce to-day not only meats, meat extracts and soups, but they manufacture lard, tallow, stearine and oleomargarine. They also produce soaps, candles and hydrogenated fats; in the manufacture of these products, they recover glycerin as a by-product. From the different parts of the animal, especially from the pancreas, the thyroid and the suprarenal glands, therapeutic agents of great medicinal

value are obtained. From the stomachs of hogs pepsin is produced and the use of the latter has been greatly increased within recent years by the clever discovery of two brother chemists, the Messrs. Wallerstein of this city, that beer of absolute chill-proof quality is obtained by the use of pepsin. The governing thought of their invention lay in the desire to keep in colloidal solution those albuminoid substances which could not be separated during the process of refrigeration; the use of a minute quantity of pepsin makes this possible.

Further by-products of the packing-houses are glue and gelatine, both products of great importance, particularly in view of the universal shortage all over the world of glue stock, and the correspondingly high prices prevailing for these products. The bones of the slaughtered animals are charred for the preparation of bone-black, which, as you know, is a valuable filtering and refining material. In other departments of the packing plants brushes are made from the bristles of the hogs. The hair is also recovered and the skins and hides go to the tanneries to be converted into leather. What is left is placed on the market as fertilizing materials, as for instance, dried blood and tankage.

Viewing these remarkable results, it is obvious that there is hardly any necessity of further legislation concerning the disposition of offal from the packing plants.

#### PAPER AND PULP INDUSTRIES

Other industries directly affected by legislation prohibiting the pollution of streams are the paper and pulp industries. Here, however, the problem of a satisfactory disposition of the objectionable materials offers greater difficulties than in most of the other industries. Some of the waste material is recovered through mechanical separators, but most of it still goes to waste, and this has resulted in the closing by law of a number of plants. A beginning towards recovery has been made through the Mueller-Kestner process whereby the spent sulfite liquors are neutralized and then concentrated in a vacuum system. The liquid thus obtained is used principally for laying dust on roads in the same manner as petroleum oils are used in this country. In Sweden attempts are being made to produce ethyl alcohol from sulfite liquors and the results are claimed to be quite satisfactory, but while these are steps in the right direction, the great problem affecting these industries still remains unsolved.

#### ETHYL ALCOHOL FROM LUMBER WASTE

In this connection, I do not think it amiss to point out another incongruity of laws as enforced in various countries and the discrimination shown against certain products. One of the greatest wastes in this country is that of the lumber industry. The waste in that particular industry is appalling and when we recall the strenuous efforts towards conservation of our natural resources, one stands aghast at the wanton waste still going on in that industry, for wherever you see a lumber mill of large capacity, you will invariably find a burner installed where such wood waste as cannot be used in the production of steam is incinerated, and millions of dollars worth of material escapes unused into the air in the form of gases. During the last years an industry has been started in this country based upon the original discovery of Classen that cellulosic materials may be converted into reducing sugars, from which ethyl alcohol may be produced. There is only one plant in operation thus far, but the results obtained seem to indicate that this new method of producing ethyl alcohol is commercially feasible and lucrative. The cash capital invested in this plant amounts to \$1,000,000. The product obtained is of the very highest grade, practically free from fusel oils and surpassing that produced in grain distilleries, yet the most natural outlet for ethyl alcohol is closed to this industry, because our laws provide that only grain distilled spirits may be used in the compounding of whiskeys. In Canada, however, no such restrictive legislation exists because there the law simply provides that ethyl alcohol may be

used, irrespective of its source. It would not be surprising, therefore, if the development of this new industry should prove speedier in Canada than in this country.

#### FERTILIZER INDUSTRY

Of much interest to chemists is a bill recently introduced in Congress by Representative Falson, of North Carolina, providing for an appropriation of \$400,000 to enable the Department of Agriculture to procure economical methods for the production of artificial fertilizers by means of electricity. It would seem that official circles have taken cognizance of the fact that saltpetre deposits in Chile are not far from complete exhaustion, and that our lawmakers have arrived at the conclusion that they can rely upon the chemist to meet the situation—producing in place of saltpetre a cheap nitrogenous fertilizing material which can be secured in unlimited quantities.

You all know that the utilization of nitrogen from the air by the combination of nitrogen and oxygen of the atmosphere with the formation of nitric acid is an accomplished fact, and is brought about either through the medium of the electric arc and the silent electric discharge, or under the influence of high electric tension. In the form of a new chemical compound, called calcium cyanamide, which is produced by combining nitrogen from the air with calcium carbide, a plant food is obtained which, as a fertilizing agent, is as efficient as Chile saltpetre or ammonium sulfate. The production of these substances from atmospheric nitrogen will, therefore, remove the anxiety of many writers on economics concerning the difficulty of feeding an ever-increasing population, owing to the gradual exhaustion of the soil.

#### SYNTHETIC PRODUCTION OF NITRIC ACID

Since nitric acid is also used largely for nitrating glycerin, cotton and cellulose, and since these nitrated products are the principal constituents of the smokeless powder and high explosives used by the armies and navies of the world, it is apparent that aside from its importance from economic considerations, a process of making nitric acid independently of Chile saltpetre will become of extreme importance in case of war, for it removes the danger of being cut off from the supply of Chile saltpetre by a hostile navy. As yet, the principal production of nitric acid from atmospheric nitrogen is centered in Norway, because that country has natural water power of a tremendous magnitude, with the further advantage of being located within easy reach of the principal markets abroad. Even in Norway, however, restrictions have been placed by law upon this new industry—the law providing that only citizens of Nor-

way may be engaged in the exploitation of these natural water powers. This caused the severance from the Norway enterprise of Dr. Schoenherr, one of the pioneers of this new industry.

#### CONCLUSION

The time at my disposal does not permit the enumeration of all that has been accomplished in the utilization of industrial wastes through the compelling force of legislation. The aniline industry, the production of sulfate of ammonia from gas residues, of coppers from pickling liquors in steel and wire works, of copper zinc and nickel from plating works, of fats and soaps from textile mills, and the products obtained in the reduction of garbage would all come under this heading. The last named subject alone is not only of the greatest importance and greatest interest, but in itself would suffice for a complete address. It is our good fortune to have been able to make an arrangement, largely through the cooperation of our fellow member, Dr. Maximilian Toch, to visit the garbage reduction plant on Barren Island, a courtesy which I understand has not been enjoyed by any other scientific or technical association. What I might say on the subject of garbage reduction, I am sure will be said in a much more comprehensive manner at the time of our visit to Barren Island, so that I believe I have your permission to leave the subject for the time being.

I believe I have shown that what may at first have seemed oppressive legislation actually developed into progressive legislation, and led to the building up of important chemical industries, which, in point of commercial value, as well as in point of direct benefit to mankind, rank second to none. And now when fears are expressed regarding the commercial and industrial future of this country because of the present tendency to disband large industrial organizations and corporations, I believe the chemist has no cause for apprehension, for it is the chemist, first of all, who is sought in times of need. His services are appreciated all the more when competition calls for a greater exercise of scientific knowledge and of technical skill. This holds good even with respect to the effects of the new tariff. While the removal of a high protective tariff may bring hardships to certain industries, the ingenuity of the chemist and chemical engineer will assert itself and lead us to conditions possibly more equitable than they have been in the past. I believe that it will always be a case of history repeating itself, and I cannot see other than a most hopeful future for the chemical industries of this country.

17 BATTERY PLACE, NEW YORK CITY

## SCIENTIFIC SOCIETIES

### TENTATIVE SPECIFICATIONS AND ANALYTICAL PROCEDURE FOR 30% HEVEA RUBBER INSULATING COMPOUND

Preliminary Report of the Joint Rubber Insulation Committee  
Appointed by a Group of Manufacturers and Users of  
Rubber Compounds, 1911-1914

A conference of manufacturers and users of rubber insulation was held at New York on December 7, 1911, upon the invitation of Mr. E. B. Katte of the N. Y. C. & H. R. R. R. Co. The following interests participated:

U. S. Signal Corps	General Electric Co.
U. S. Bureau of Standards	Hazard Manufacturing Co.
American Chemical Society	Simplex Wire & Cable Co.
New York Central Lines	Standard Underground Cable
Pennsylvania R. R.	Co.

Major S. Reber, of the U. S. Signal Corps, was elected chairman.

Attention was called to the diversity of the specifications and methods of analyzing rubber insulation then in vogue, and it was suggested that steps be taken to improve and standardize them. After full discussion, it was decided to appoint a Committee to devise specifications and an analytical procedure for rubber insulating compounds. The report of this committee, which is known as the Joint Rubber Insulation Committee, is presented herewith.

The committee has consulted the available literature on rubber analysis and has also obtained assistance and advice from chemists interested in this field of work. Some of the details in the methods of analysis were taken directly from the work of others when such action was warranted by the experimental results obtained, and in certain cases modifications were made in available methods. In some cases the methods adopted constitute distinctly new features in rubber analysis.

The committee desires to express its thanks, especially to



Messrs. D. A. Cutler, F. Dannerth, F. S. Deemer, F. A. Hull, M. M. Kahn, G. H. Savage and D. Whipple.

Sub-Committee on Publication of Report { W. A. DEL MAR  
P. POETSCHKE  
E. L. WILLSON

#### PART I GENERAL REPORT

At the conference of December 7, 1911, it was resolved that a committee be appointed to develop a means of specifying and analyzing rubber insulation, the committee to report its findings at a future conference.

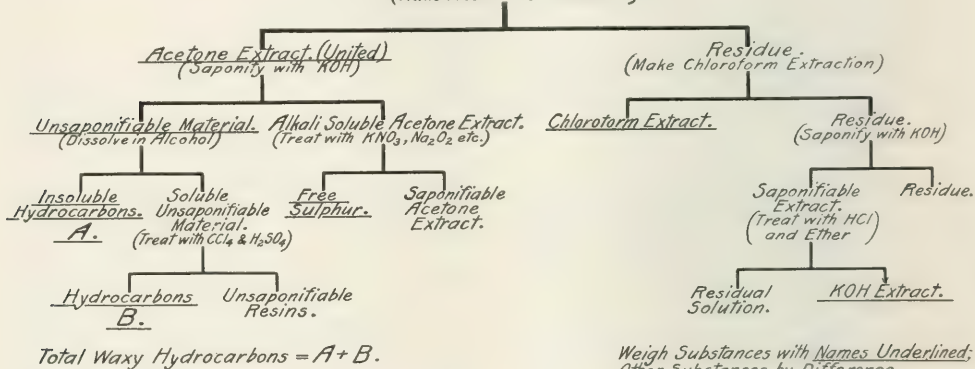
The chairman of the conference, assisted by other members, appointed the following to serve upon this committee: C. R. Boggs, Simplex Wire & Cable Co.; W. S. Clark, General Electric Company; W. A. Del Mar, W. B. Geiser, N. Y. C. & H. R. R. R. Co.; J. P. Millwood, consulting chemist; P. Poetschke, Lederle laboratories; H. B. Rodman, Pennsylvania R. R. Co. Later, at the request of the committee and by unanimous consent of the members of the original conference, the following were added: J. B. Tuttle, U. S. Bureau of Standards, and E. L. Willson, Hazard Manufacturing Company. The committee thus con-

siders not perfect and believes that it should be put into use for a year before being offered as final. With this in view the committee hereby presents to the conference a preliminary procedure and requests the permission of the conference to publish it and obtain the results of experience with it during the ensuing year. The committee proposes to avail itself of the experience gained in this year and to incorporate whatever improvements it may decide upon in a final report.

The committee has also made a study of specifications for rubber insulating compound. It presents herewith a chemical specification for a compound containing 30 per cent of Hevea rubber with mineral fillers and requests that this specification, like the analytical procedure, be considered as tentative.

There may still exist the possibility of making compounds which will conform to the specifications when analyzed by the procedure, but which are not compounded as desired. The committee believes, however, that the probability of such compounds being supplied is very small indeed. After more experience with the procedure it may be possible to narrow the limits prescribed in the specification.

#### Two 2 grm. Samples of Rubber. (Make Acetone Extractions)



#### Rubber Analysis. Exclusive of Fillers and Total Sulphur Determinations. Outline of Method.

stituted is composed of three railroad men, three independent chemists and three representatives of the manufacturers. Of the nine members, seven are chemists and two are engineers.

The committee, immediately upon its formation, decided to confine itself to the development of a specification and an analytical procedure for compounds of the 30 per cent Para type. In accordance with this policy it considered the available analytical procedures and developed several which formed the basis of further study. Samples of different rubber compounds were analyzed by these tentative methods. The results were unsatisfactory and the discrepancies were investigated. Sub-committees were formed to do much of this work. Twelve regular committee meetings, besides numerous sub-committee meetings, were held; thirteen different compounds were distributed to be analyzed by the entire committee, and many more compounds were experimented upon by the sub-committees and individual members.

The outcome of this work has been a gradual elimination of errors and the development of a procedure which, with experience, will give uniform and consistent results.

The committee feels that the procedure which it has developed

#### PART II. PROCEDURE FOR THE ANALYSIS OF RUBBER COMPOUND

OBJECT—The object of this procedure of analysis is to determine whether rubber compounds comply chemically with the accompanying specification, which is intended to secure compounds containing 30 per cent of the best Hevea rubber and mineral fillers.

OUTLINE OF PROCEDURE—The general procedure is shown by the above diagram, which gives an outline of the separations to be affected by acetone and chloroform extractions, and saponification with alcoholic potash.

GENERAL—Make the analysis upon the insulation after vulcanization and, whenever possible, before the saturation of the braid. Wipe the insulation thoroughly with a damp cloth to remove any adhering material, but do not remove waxy hydrocarbons from the surface.

If, however, a saturated braided sample must be used, remove the braid and sandpaper the insulation to a depth of at least 5/1000 of an inch and wipe with a damp cloth. In such cases report the condition of the sample.

Perform all determinations in duplicate and take the average

value arbitrarily as the true value. Duplicate determinations must check within the limits specified.

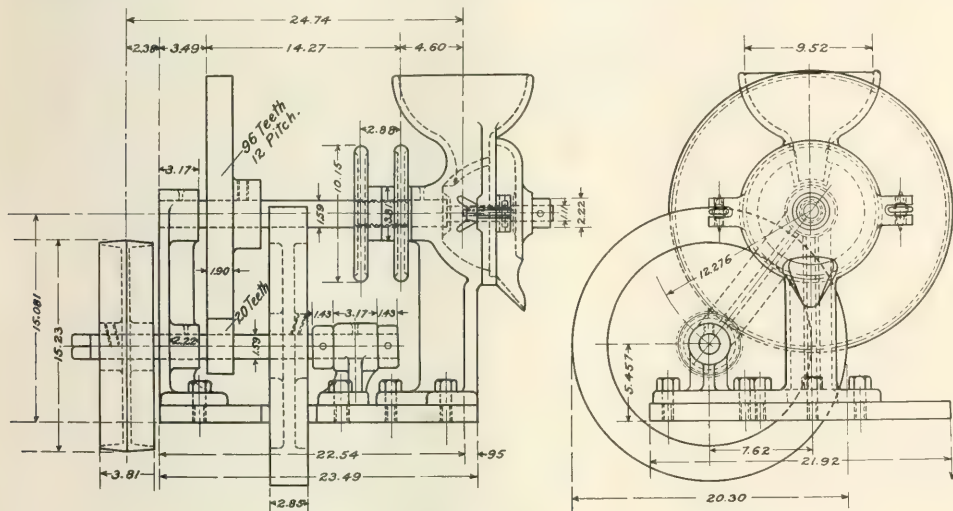
Make blanks on all determinations and deduct the result accordingly.

**SAMPLE**—Remove the insulation entirely from sufficient wire to give a sample weighing about 25 grams. Cut this into small strips and grind slowly in either a No. 0 Enterprise coffee mill or a mill such as shown by the diagram below. Adjust the grinder so that not more than 20 per cent will pass through a 40 mesh sieve. Sift all the material through a 20 mesh sieve, regrounding what is retained on the sieve until the entire sample has passed through. The wires of the sieve shall be evenly spaced in both directions and shall be of 0.016 and 0.010 inch diameter in the 20 and 40 mesh sieves, respectively. Remove with a strong magnet any metal that may have come from the grinder and thoroughly mix the sample.

**EXTRACTION APPARATUS**—The extraction apparatus shall conform with the diagram on page 78. It shall be heated

Desiccate until cool and weigh. Continue to dry for 2 hour periods until constant weight is obtained. In drying, place the flask on its side but at a sufficient angle from the horizontal so that the extract does not appreciably run down the side of the flask.

**UNSAFONIFIABLE MATERIAL**—Add to the acetone extract 50 cc. alcoholic KOH solution, boil under a reflux condenser for two hours, and evaporate to dryness, removing all alcohol. Add 10 cc. water and 20 cc. ether, heat until the wax, etc. are in solution; cool, transfer to a separatory funnel, wash out the flask with warm water and, when cool, finally with two 20 cc. portions of ether. The water volume should be 100 cc. and the ether at least 40 cc. Shake vigorously for two minutes, and allow the solutions to separate thoroughly. Draw off the aqueous solution into a second funnel, leaving in the first funnel the ethereal solution and any flocculent material that may be present. Again rinse the flask with 20 cc. ether and add it to the aqueous solution; shake vigorously for two minutes, and when separated draw



*Grinding Plates of the No. 0  
Enterprise Coffee Mill to be used.*

**RUBBER GRINDER**  
*All dimensions in Centimeters.*

so that the period of filling an empty siphon cup with acetone and completely emptying it will be between 2½ and 3½ minutes.

**PREPARATION OF REAGENTS**—Acetone shall be freshly distilled over anhydrous  $K_2CO_3$ , using the fraction 56–57° C.

Alcoholic KOH solution shall be of normal strength and shall be freshly made by dissolving the proper amount of KOH (purified by alcohol) in 95 per cent alcohol which has previously been distilled over KOH. The solution shall be allowed to stand for 24 hours and only the clear liquid used.

Ether shall be washed with three successive portions of distilled water and distilled, using the fraction 34–36° C.

Chloroform shall be pure and freshly distilled.

Carbon tetrachloride shall be pure and freshly distilled.

Reagents not otherwise specified shall be C. P.

**ACETONE EXTRACTION**—Extract continuously with 60 cc. acetone for eight hours, two 2 g. samples that have been prepared within 24 hours. Unite the extracts in a weighed flask, using hot chloroform to rinse the flasks. Distill off the reagents and dry the flask and contents for four hours at 95–100° C.

off the aqueous solution and unite in the first funnel the ethereal solutions and any flocculent material. Repeat, shaking with 20 cc. portions of ether until the extraction is complete, using at least 120 cc. ether. Wash the flask and the funnel, from which the ethereal solution has been taken, with water, until they are free from alkali, subsequently using this wash water to wash the ethereal solution. Continue washing with water until it has been washed twice after it shows no alkaline reaction. Retain with the ethereal solution any flocculent material. Filter the ethereal solution from the flocculent material, through a small pellet of extracted cotton, into a weighed flask, washing first with ether and subsequently with hot chloroform, using this to rinse the original flask and both separatory funnels. Evaporate the solvents and dry the extract to constant weight at 95–100° C.; desiccate until cool and weigh.

**HYDROCARBONS A.**—Add 50 cc. absolute alcohol to the unsaponifiable material and warm until solution is as complete as possible. Cool the solution to –4 or –5° C. and maintain at this temperature for one hour by packing the flask in a mixture of ice and salt. Filter out the waxy hydrocarbons, using a fun-





until it is thoroughly washed. Filter and wash well with benzol. Wash in the same manner both beakers with hot alcohol and then transfer the residues to the filter paper, using hot alcohol and an acetone extracted policeman. Wash finally with acetone. Dry in air at 95–100° C. and weigh. Again wash the filter paper and contents with benzol and alcohol, dry, weigh and repeat this treatment until constant weight is obtained. Evaporate all the filtrates and washings, transfer to a porcelain dish, burn off and weigh. Add this amount to the fillers found above. If this ash is greater than 1 per cent, the entire determination shall be repeated. Subtract 0.5 per cent as an arbitrary value for the amount of organic matter from the rubber retained with the fillers.

**SULFUR IN FILLERS**—Transfer the fillers from the filter paper into an iron crucible; burn the filter paper and add the ash to the crucible. Add the Total Sulfur flux and proceed with the determination of sulfur as in the next paragraph. Subtract the percentage of sulfur found from the percentage of fillers to determine the percentage of fillers free from sulfur.

**TOTAL SULFUR**—Mix a 0.5 g. sample with 4 g.  $\text{Na}_2\text{O}_2$  and 6 g.  $\text{K}_2\text{CO}_3$  in a dry 15 cc. iron crucible. Cover and heat gradually until the mixture fuses, proceeding cautiously as rapid heating will cause an explosion, and then bring to quiet fusion for 15 to 20 min. Apply the heat so as to avoid contamination with sulfur fumes. Rotate the crucible while the melt solidifies. When cool, put crucible and cover into a casserole containing 200 cc. of water; add 5–10 cc. bromine water and boil until the melt is dissolved. Allow the precipitate to settle, decant the liquid through a thick filter and wash the residue with hot water. Acidify the filtrate with HCl, evaporate to dryness and dehydrate silica; add 2 cc. conc. HCl, take up in water, filter and wash, making the total volume about 400 cc. Heat to boiling and add slowly a slight excess of hot 10 per cent  $\text{BaCl}_2$  solution. Allow to stand over night, filter, wash, ignite, weigh the  $\text{BaSO}_4$  and calculate to sulfur.

**SPECIFIC GRAVITY**—The specific gravity shall be the ratio of the weight of a given volume of the rubber, to the weight of an equal volume of water, both at 20° C. Cut strips of the largest applicable size from the conductor and use about 5 g. for the sample. Determine the specific gravity in the usual manner by means of a specific gravity bottle. Care must be taken that no air bubbles adhere to the sample.

**CHECKS**—Duplicate determinations shall check within the following limits expressed as percentages of the original sample:

DETERMINATIONS	Limits for checks
Acetone Extract.....	0.10
Saponifiable Acetone Extract.....	0.10
Unsaponifiable Resins.....	0.10
Waxy Hydrocarbons.....	0.10
Free Sulphur.....	0.05
Chloroform Extract.....	0.10
Alcoholic Potash Extract.....	0.10
Fillers, free from sulfur.....	0.50
Total Sulfur.....	0.10
Specific Gravity.....	0.01

**INTERPRETATION**—The Rubber shall be considered to be the difference between 100 and the sum of the Waxy Hydrocarbons, Total Sulfur and the Fillers (free from sulfur), expressed as percentages. If the Chloroform Extract is over 3.0 per cent of the rubber so calculated, subtract the excess from the Rubber. If the KOH extract is over 1.8 per cent of the Rubber, as first calculated, subtract this excess also from the Rubber.

**CARBON AND RED LEAD**—Heat about 1 g. of the sample with 30 cc. conc.  $\text{HNO}_3$  and 15 cc. water. A black insoluble residue indicates the presence of carbon.

When the rubber is dissolved, in the fillers determination, the absence of any red particles indicates the absence of red lead. If red particles are present, dissolve another sample by the same

method as for fillers, filter the solution into a Gooch crucible and wash thoroughly. Remove the felt and a residue to distilling flask, add HCl and distill over the chlorine liberated by the lead peroxide, absorbing the gas in a solution of KI and starch. Not more than 0.1 cc.  $\text{N}/10$  thiosulfate shall be required to titrate the iodine liberated.

**STATEMENT OF RESULTS**—The results of the analysis shall be stated in the following form:

	Per cent
Acetone extract.....	
Saponifiable acetone extract.....	
Unsaponifiable resins.....	
Waxy hydrocarbons.....	
Free sulfur.....	
Chloroform extract.....	
Alcoholic potash extract.....	
Fillers free from sulfur.....	
Total sulfur.....	
Rubber.....	
Color of acetone extract (60 cc. vol.).....	
Fluorescence in acetone extract solution (present or absent).....	
Hydrocarbons A (consistency and color).....	
Hydrocarbons B (solid or liquid).....	
Color of chloroform extract (60 cc. vol.).....	
Carbon (present or absent).....	
Red lead (present or absent).....	
Specific gravity.....	

### PART III. EXPLANATION OF PROCEDURE

**GENERAL**—The committee felt the more acceptable solution of its problem of drawing up a procedure which would give the percentage of rubber present in a compound with a reasonable degree of accuracy, to be the perfection and amplification of the difference method rather than the development of a direct method, which, if equally correct, might not inspire confidence because of the comparative novelty of its application to this purpose.

The most feasible means of limiting the kind of rubber was considered to be the determination of the saponifiable and unsaponifiable resins. These are fairly constant characteristics of the resins of Hevea rubber, and of compounds made from the same. Other methods, such as the determination of the saponification number and the optical activity of the resins, were thought to be unpracticable.

The method as developed is applicable to the analysis of any pure rubber compound containing only mineral matter with or without ceresine or paraffine wax, regardless of the kind or amount of rubber, and can be used in conjunction with other specifications, provided the limits are changed to correspond with the amount and kind of rubber desired, and due consideration is given to interfering mineral matter. When applied to a compound without ceresine or paraffin wax the unsaponifiable acetone extract is the unsaponifiable resins.

The method has been definitely described, to make it certain that experienced chemists may obtain concordant results. The interpretation has been rigidly defined, obviating any ambiguity as to the meaning that will be assumed, even though this sometimes appears to be arbitrary.

**SAMPLE**—In order to obtain uniform results, the Committee has established, by experiment, that a definite method of sampling has to be adopted and that for all extractions the sample must be reduced in a prescribed manner to at least an approximately similar degree of fineness. For this reason the procedure specifies a definite type of grinder obtainable in two forms, and also specifies definite sieves.

**EXTRACTION APPARATUS**—The committee has proved that the extraction apparatus used by different chemists must be of exactly the same form and the same size. It was also proved that small samples in the apparatus give the maximum results and that the rate of extraction is dependent upon the amount of solvent and its temperature as it passes through the sample. The apparatus finally adopted combines the advantages of

several forms that were studied and together with simplicity of operation and adjustment to uniform conditions, gives practically complete extraction when used as specified. A number of other variations that might have a possible effect upon the amount of extract were tried but their effects were found to be inappreciable.

**ACETONE EXTRACTION**—The extraction is made within 24 hours of the preparation of the sample, so obviating any appreciable oxidation. Two samples are extracted and united, so that a larger amount of extract may be obtained for the subsequent separations, and the extraction apparatus kept within a convenient size. Hot chloroform is used to facilitate the complete transference of the extract. The flasks are placed on their sides when drying to hasten the emission of the solvent and thus reduce chance of volatilizing, through longer heating, some of the more volatile constituents of the extract. Drying *in vacuo* at room temperature does not remove all the moisture if paraffin is present and such drying with heat or at 100° C. in an inert gas, presents no practical advantage over the method given.

**SEPARATION OF THE ACETONE EXTRACT**—The method given was developed so that all the desired constituents could be determined in one sample.

Emphasis is laid on thorough extraction of the unsaponifiable material and the retention of the flocculent material with the ethereal solution. This latter material is not soluble in either ether or water, but it was proved that if such as was chloroform-soluble were included in the unsaponifiable material, the subsequent determination of the hydrocarbons would be more exact. A portion of this flocculent material is insoluble in chloroform.

The hydrocarbons are determined in two places, making an approximate separation between the solid and the liquid ones, if both are present. The first hydrocarbons (A) are those insoluble in the solvent at a low temperature. The presence of unsaponifiable resins in the solution prevents the more complete freeing out of the hydrocarbons, but the remainder is obtained after treatment of the resins with sulfuric acid. In this way, chance of loss through the action of the acid has been largely eliminated.

The method for free sulfur gives all the sulfur in the acetone extract with the exception of negligible amounts which may be in the unsaponifiable material. It was proven that the results agree with determinations made directly on other acetone extracts.

The saponifiable and unsaponifiable resins are obtained by difference.

**CHLOROFORM EXTRACTION**—The chloroform extraction should be made at once after the acetone extraction, or the sample put in a vacuum, so as to avoid the danger of an abnormally high extract. When the extract is dried as specified, constant weight is obtained before any appreciable oxidation occurs. If bituminous substances are present, that portion which has not been extracted by the acetone will be largely soluble in chloroform and can be readily distinguished by its color. The amount of extract is also affected by the presence of uncured rubber and rubber of low degree of polymerization. A properly cured Hevea compound will always give a little extract with chloroform, which varies somewhat with the method and conditions of cure.

**ALCOHOLIC POTASH EXTRACTION**—The alcoholic potash extraction is the usual saponification process for obtaining the fatty acids of rubber substitutes. The total amount of such substitutes is not obtained, but if any appreciable amount is present, the value will exceed that of the limit allowed. When no substitutes are present, this determination always yields a small amount of extract from Hevea rubber.

**FILLERS**—Since the rubber is determined by difference, it is necessary to determine the amount of fillers. Ashing the com-

pound gives accurate results provided no volatile or decomposable fillers are included. This, however, cannot be assumed to be the case. The determination of fillers by using solvents to dissolve the rubber has always presented a difficult problem and it is only after a great many experiments that the committee can report a reasonably satisfactory method.

Many kinds and probably every class of rubber solvents were tried, with the result that some did not completely dissolve the rubber at low temperatures and ordinary atmospheric pressure; others appeared to dissolve the rubber but formed a colloidal solution holding some of the fillers which could neither be filtered nor centrifuged clear of mineral matter; the ones that did not present these difficulties consumed much time.

Terebene was found to be the solvent which would most completely dissolve the rubber and after continued heating would completely destroy the rubber in solution as such, and so break up the colloidal solution. Filtering out the mineral matter is then a comparatively simple process. The treatment with terebene must be performed in the presence of air to break up the colloidal solutions. A disadvantage of using terebene is the length of time required to obtain satisfactory solution. The speed is greatly hastened if at first xylol is used with the terebene. After decanting this solution, terebene is used alone. The rapidity of the action is also hastened by increasing the temperature. The specified gives reasonable speed without serious danger of carbonizing the rubber or of losing any of the fillers by decomposition.

It was proved that there is organic matter derived from the rubber, which is insoluble in the solvents and remains with the fillers. Without taking this into account, the fillers will appear high, and the rubber by difference, low. As this organic matter was proved to be largely proteid matter, and this was originally a part of the rubber, an allowance is made for it. This is the amount generally retained when the method is carried out as specified. It is possible, by centrifuging, to throw out of the solution a great deal more than this, and it is also possible to determine the approximate amount retained in each case, but the slight increase in accuracy does not justify the extra determination.

Most of the details of this procedure are self-evident, but it is probably worthy of note that the benzol solutions are filtered into a separate beaker, as otherwise the benzol is apt to precipitate, from the terebene solution, organic matter which may be mistaken for mineral matter or conceal mineral matter passing through the filter. The filtrates are ashed since traces of mineral matter are always found in them. Emphasis must be laid upon the necessity of conducting blanks on the solvents.

**SULFUR IN FILLERS**—The sulfur in fillers is determined in order to calculate the rubber by difference. It is carried out only on the fillers contained on the filter paper, the sulfur in the ash from the filtrate and washings being negligible.

**TOTAL SULFUR**—Several methods for total sulfur were tried. The method given was found to yield accurate results.

**INTERPRETATION OF RESULTS**—Emphasis is laid on the method of calculating the results. The saponifiable acetone extract and the unsaponifiable resins are considered to be parts of the rubber. The chloroform and alcoholic potash extracts, when within the limits specified, are likewise so considered. It has been explained that the proteid matter with the fillers has been allowed for, since it is also a part of the rubber. The fillers are calculated sulfur-free, so that the sulfur will not be subtracted twice. No allowance is made for the ash in the raw rubber as it is considered to be negligible. This method of calculation has to be adopted if the rubber found is to agree with that originally put into the compound.

**MOISTURE**—A determination of moisture is not given, as electrical tests will detect its presence if in excess. If electrical tests

are required, the error introduced by the omission of this determination is very small.

*Note*—With a procedure of this length it is impossible to explain every detail without undue elaboration and the Committee wishes to point out that while to experienced chemists the procedure may seem overburdened by detail, yet every specified detail was found necessary in order that the conditions essential to accurate and consistent work might be reproduced by all chemists using the procedure. For this reason it is extremely important that all instructions be observed even if their significance is not perceived by the individual chemist. It will probably be found that even with the instructions properly observed, some experience will be needed to apply the method successfully.

#### PART IV. TENTATIVE SPECIFICATION FOR 30 PER CENT RUBBER COMPOUND

A 30 per cent fine Para or smoked first latex Hevea rubber compound with mineral base shall be furnished. It shall contain only the following ingredients: Rubber, sulfur, inorganic mineral matter, and refined solid paraffin or ceresin.

It shall not contain either red lead or carbon.

The vulcanized compound shall conform to the following requirements, when tested by the procedure which forms a part of this specification.

(a) Results to be expressed as percentages by weight of the whole sample:

	Maximum	Minimum
Rubber.....	33	30
Waxy hydrocarbons.....	4	
Free sulfur.....	0.7	

(b) Results to be taken between the limits given in proportion to the percentage by weight of rubber found:

	Limits allowed	
	Maximum	Minimum
For 30 per cent Rubber Compound:		
Saponifiable acetone extract.....	1.35	0.55
Unsaponifiable resins.....	0.45	
Chloroform extract.....	0.90	
Alcoholic potash extract.....	0.55	
Total sulfur (see note 3).....	2.10	
Specific gravity.....		1.75
For 33 per cent Rubber Compound:		
Saponifiable acetone extract.....	1.50	0.60
Unsaponifiable resins.....	0.50	
Chloroform extract.....	1.00	
Alcoholic potash extract.....	0.60	
Total sulfur (see note 3).....	2.30	
Specific gravity.....		1.67

The acetone solution shall not fluoresce.

The acetone extract (60 cc.) shall be not darker than a light straw color.

Hydrocarbons shall be solid, waxy and not darker than a light brown.

Chloroform extract (60 cc.) shall be not darker than a straw color.

Failure to meet any requirement of this specification will be considered sufficient cause for rejection.

*Note 1*—Contamination of the compound, such as by the use of impregnated tapes, will not excuse the manufacturer from conforming to this specification.

*Note 2*—This specification shall be supplemented by appropriate clauses relating to tensile strength, elasticity, insulation resistance and dielectric strength.

*Note 3*—The limit of total sulfur may be omitted at the option of the purchaser (see Part V).

#### PART V. EXPLANATION OF SPECIFICATION

Experience has shown that compounds which upon analysis show the characteristics of good Hevea rubber, may be relied

upon to be more permanent than those made of rubber of other grades. It is not affirmed by the committee that a compound which conforms with this specification, is necessarily permanent, or that a better compound cannot be made, but it is believed that enforcement of the specification will limit the use of inferior materials and that it will put the manufacturers more nearly upon an equality of endeavor, where they can use their experience to obtain the best results. Used in connection with the analytical procedure, the specification will enable purchasers to order a good compound and to ascertain with a greater certainty than heretofore, whether the material received represents the compound specified.

The term Hevea applied to rubber means rubber from the *Hevea Brasiliensis* tree whether wild or cultivated and regardless of the locality in which it has been grown. Para rubber is Hevea rubber which has been shipped from the port of Para, Brazil, and comes in several grades. Smoked first latex Hevea rubber is a high grade of plantation rubber which is collected prime and consists entirely of rubber which has risen in the settling vats. It is coagulated chemically and smoked in order to give it a hard cure, which ensures the greatest durability. The rubber required by this specification should be Hevea rubber of good quality, such as fine Para or smoked first latex.

Carbon is excluded because it is considered, by some purchasers, to be deleterious.

Red lead is excluded because of the possibilities of its deleterious effects on the rubber.

Ozokerite is prohibited because the acetone extract obtainable from it interferes with the separation of the acetone extract obtainable from the rubber, thereby vitiating the assay of the rubber extract. This prohibition is unimportant to the manufacturers, as ceresin, which is permitted, is the essential constituent of ozokerite.

An upper limit is placed upon the rubber in order to prevent the attainment of electrical and mechanical strength by the use of an extra quantity of inferior rubber whose lasting qualities might not be satisfactory.

The hydrocarbons are limited, owing to their tendency to separate from the compound and thus possibly cause porosity.

The free sulfur is limited because an excessive amount may be deleterious.

The maximum limit on the saponifiable acetone extract is to prevent the use of raw or reclaimed rubber with high saponifiable extract. The minimum assists in forcing the use of Hevea rubber, since it is characteristic of the acetone extract from Hevea rubber to be largely saponifiable.

The unsaponifiable resins are limited because a low proportion of unsaponifiable resins is characteristic of Hevea rubber. A high result might be due to the presence of reclaimed rubber.

The chloroform extract is limited, first to prevent the use of bituminous substances, and second, to limit depolymerized and under-cured rubber.

The alcoholic potash extract is limited to prevent the use of saponifiable rubber substitutes.

The specific gravity is limited to reconcile the specifications of ingredients by weight with the practice of purchasing material by volume.

Fluorescence of the acetone solution is prohibited as it indicates the presence of mineral oils.

The color of the acetone extracts is specified to conform with the normal color of the extract from Hevea rubber. A darker color indicates adulteration or an inferior grade of rubber.

The hydrocarbons are required to be solid in order to prevent the use of oils and paraffin of low melting point. The shade required is that obtained from paraffin wax or 'ceresins'. If hydrocarbons B are liquid this would indicate reclaimed rubber softened with mineral oil, or a poor grade of paraffin.

The color of the chloroform extract is specified to conform



with the color of dissolved gum in minute quantities. The presence of bituminous substances would be indicated by a brown or black color.

It would be desirable that the sulfur of vulcanization be limited to exclude reclaimed rubber, which contains the sulfur of its previous vulcanization, but the committee has not yet developed an acceptable method for determining this quantity. It is therefore, confronted with the choice of either placing a limit on the total sulfur or giving up the attempt to exclude shoddy by sulfur limitations. Option is therefore given to the purchaser to insert or omit the limit on total sulfur. Such insertion will at times exclude reclaimed rubber and the committee believes it possible to make a suitable compound with this limitation. The committee thinks that a sulfur limit positively excluding reclaimed rubber, would place too great a hardship, in other ways, on the manufacturers. Where the specification

is used with no total sulfur limit, the use of many kinds of, or much, reclaimed rubber, will be guarded against by the limits of the various components of the acetone extract. When the limitation on total sulfur is omitted, sulfur-bearing fillers, which possess certain advantages, may be used.

This specification should be supplemented by appropriate elasticity and tensile strength tests, in order to add to the assurance that good rubber has been used and that the vulcanization process has been properly carried out; also by appropriate electric stress and resistance tests, to assure proper insulating qualities and homogeneity of structure. The exact values of the limits for these tests will depend upon the use to which the material is to be put.

JOINT RUBBER INSULATION COMMITTEE  
W. A. DEL MAR, *Secretary*

OCTOBER, 1913

## NOTES AND CORRESPONDENCE

### OZONE

*Editor of the Journal of Industrial and Engineering Chemistry:*

In the November issue of THIS JOURNAL, Mr. Buswell concludes from the papers of Jordan and Carlson, and of Sawyer and the Misses Beckwith and Skolfield, in the *Journal of the American Medical Association*, that the use of ozone as an adjunct in ventilation has been proven totally unjustifiable. In so far as ozone is expected to sterilize the air, Mr. Buswell is correct, but when he concludes that ozone has no function whatever in ventilation, and that its harmfulness and inutilty have been demonstrated, he is in error.

Ozone is applied to ventilation for the purpose of destroying odors which result from the presence of people, animals and decaying organic substances. Its value is demonstrated in numerous cases where it has stood the empirical test of giving satisfaction to the user, and by researches conducted under actual working conditions. Its application is suggested in the first place by the logical expectation that it will destroy offensive odors in crowds, because it does this in the laboratory, and because this is in accordance with the theory of the chemical action of ozone.

Following the practical demonstration of satisfactory results from the employment of ozone, it was natural and proper that physiologists should have endeavored to demonstrate whether or not ozone were capable of harmfully affecting people exposed to its influence, and accordingly numerous attempts have been made to settle this question. The evidence to date is that no single instance of harm from the use of ozone in the quantities recommended has been published, but, on the contrary, numerous efforts to prove its harmfulness have been unsuccessful. Jordan and Carlson fail utterly to show any harm to the animals exposed to weak concentrations of ozone, and are driven to the dubious expedient of insinuating that harm might result after fifty years of exposure. The same line of reasoning might be applied with equal logic to the use of electric lights, subways and prepared breakfast foods. On the other hand, Leonard Hill states that no one could unconsciously be poisoned by ozone, as the danger signals are clearly set, and that no one could remain in an atmosphere too strong with ozone. He states, moreover, that the only penalties from breathing too strong ozone for a short period are a slight irritation of the mucous membranes and perhaps a headache.

The writer has had considerable experience with ozone and has observed numerous co-workers who, with himself, have been exposed during five years to various concentrations of ozone, which, according to the authors above quoted, should have proven highly injurious if not fatal, but he has never noted the

least ill effect from repeated and often prolonged exposures to these relatively high concentrations.

The bacteriological experiments referred to are of little or no interest, for two reasons: *First*, Because they are in accordance with what is already well known; *Second*, Because sterilization of the atmosphere is not of any value whatever in sanitation. Few sanitarians believe that diseases are transmitted by bacteria in the air; therefore the fact that ozone will not destroy bacteria in the air is entirely aside from the question and no disqualifier of ozone.

Regarding the experiments with animals on which tracheotomy had been practiced, and into whose lungs ozone, in concentrations of from twenty to fifty times the concentrations recommended for ventilation purposes, had been directly introduced, we can say that the results might have been predicted, and that they have no bearing on the question of ozone in ventilation. Jordan and Carlson themselves point out that ozone, as used in ventilation, does not get into the lungs, but is absorbed in the nasal passages. They admit that it does not follow that, because strong concentrations of ozone are poisonous, weak concentrations are also poisonous, and further, they prove this to be the case in their experiments.

Referring to the efforts that were made to prove that ozone masks and does not destroy organic odors, it can be said that experiments carried on in a room such as Jordan and Carlson used, are subject to, at least, one great source of error, namely: condensation and absorption on the walls and heterogeneous objects in the room. Bail has studied this and points out that *after-odors* may be referred to this cause. Czaplewski and also Van Kupffer have dwelt on this source of error. I have experimented personally and also have had tests conducted by others qualified to make precise observations, with what appears to be a more accurate method, namely: with clean glass bottles in which the surfaces could be washed free from adhering emanation, and the results have shown that organic odors generally are destroyed, and not masked by ozone.

Jordan and Carlson contend that the removal of odors is vicious as destroying an indicator of contaminated atmosphere, but, as is generally known, there are no poisons in vitiated air, and odor exists as odor alone and as such constitutes a nuisance whose destruction vouchsafes a most important function to ozone in ventilation.

As a matter of fact, the main attack on ozone is based on two implied premises both notoriously discredited, *vis.*: (1) that there are organic poisons in vitiated atmospheres which are indicated by odors, and (2) that dry floating bacteria in the air are active agents of contamination.

It is conceded that bacteria in the air are of little or no im-

portance in sanitation; that organic poisons do not exist; that odors are a nuisance. It has been shown that ozone removes these odors, and while it has been demonstrated that in strong concentrations ozone destroys these odors, many writers, including Jordan and Carlson, persist in the unsupported allegation, that in weak concentrations, ozone although admittedly banishing them, merely masks these odors.

Wide experience attests that ozone improves the condition of the air, and inasmuch as all attempts have failed to prove the least harmfulness of ozone when properly used, its utilization is as fully justified as is the use of such empirical remedies as, for instance, colchicum in gout.

MILTON W. FRANKLIN

188 NORTH WALNUT ST.,  
EAST ORANGE, N. J.

### PLATINUM THIEF

*Editor of the Journal of Industrial and Engineering Chemistry:*

We desire to call the attention of the Society to the recent theft of platinum from this laboratory. The party suspected is a man calling himself Harry E. Newton and representing himself as a graduate of the Rolla School of Mines at the University of Missouri, '99. He claims to have been connected with

smelter work in Southern Mexico and also with the rubber industry in that country.

He is a man approximately 35 years of age, 5 feet 5 inches in height and weighing about 135 pounds. His complexion is dark and when last seen he was smooth shaven, with a face showing marks of considerable exposure to the weather. He has the appearance of a man addicted to the use of drugs in some form.

We have communicated with the secretaries of the four nearby sections and would be glad to receive any information as to his present whereabouts.

WILLIAMETTE PULP AND PAPER COMPANY

OREGON CITY, OREGON

DECEMBER 1, 1913

### RECOVERY OF IODINE FROM THE WASTE LIQUOR IN COPPER TITRATIONS

*Editor of the Journal of Industrial and Engineering Chemistry:*

The waste liquors obtained from copper titrations by the iodide method contain large amounts of iodine. This may be recovered by adding hydrogen peroxide (a few cc. of 30 per cent to about 2.5 liters). The free iodine is precipitated at once and can be easily separated by filtration.

GREGORY TOROSSIAN

11014 DETROIT AVE., CLEVELAND, O.

NOVEMBER 20, 1913

## PERSONAL NOTES

Provost Edgar F. Smith, of the University of Pennsylvania, has been elected a member of the Board of Trustees of the Carnegie Foundation for the Advancement of Teaching, to succeed Dr. Ira Remsen.

Dr. F. W. Frerichs, of St. Louis, was awarded the Medal of the American Institute of Chemical Engineers at the 6th Annual Meeting in New York, on account of his papers on "Problems in Chemical Engineering."

Dr. Bernard Herstein, formerly Chemical Expert for the Tariff Board, has gone to the Philippines to take up his new duties as Insular Collector of Customs.

Dr. Carl L. Alsberg and Dr. A. L. Winton, of the Bureau of Chemistry, have been elected Honorary Members of the Philadelphia College of Pharmacy.

The General Electric Company Research Laboratory at Schenectady is about to move into a new building specially designed for its use and in which about 50,000 square feet of floor space are devoted to experimental work.

Caswell A. Mayo, Editor of the *American Druggist*, has been elected President of the American Pharmaceutical Association.

Mr. Heinrich J. Freyn, formerly Consulting Engineer of the Gas Engine Department of the Allis-Chalmers Manufacturing Company of Milwaukee, has recently joined the H. Koppers Company of Chicago in the capacity of 3rd Vice-President.

The Chemists' Club of New York has received and is preparing for use the Friedrich W. C. Schniewind Library which consists largely of complete journal sets covering the field of coal, coke, gas and by-products of the coal gas industry.

Prof. L. B. Mendel, of Yale University, spoke on "Food Fads" under the auspices of the Washington University Chapter of Sigma Xi, St. Louis, on December 5, 1913.

Prof. Alfred H. White, of the Chemical Engineering Department of the University of Michigan, addressed the Detroit Section of the A. C. S. on Nov. 28, 1913, his subject being "Under what Circumstances can Portland Cement be Considered a Reliable Building Material for Permanent Structures?"

Dr. Sidney Born, of New York, has recently accepted the position of Director of the Laboratories of the Wm. J. Lemp Brewing Co., St. Louis.

Mr. Henry Sellman, engineering specialist in pebble mills

and grinding installations, has been employed by the Abbé Engineering Co. This company has purchased the Sellman Mill Co. business and that of Geo. M. Ball & Son, manufacturers of pulverizing and grinding machinery.

Prof. Alexander Smith was to have assumed the duties of head of the Department of Chemistry in Princeton University in the autumn of 1914. By consent of both parties, Prof. Smith's acceptance of the position has now been withdrawn, and he will remain at Columbia University.

G. S. Fraps, President of the Association of Official Agricultural Chemists, delivered his presidential address before the 13th Annual Meeting in Washington, Nov. 18, 1913, on the subject, "Progress of the Chemistry of Agriculture." This address is printed in full in the Nov. 29th issue of the *American Fertilizer*.

Dr. John A. Wilkinson, formerly at Ohio State University, is now at Missouri State University as head of the Department of Analytical Chemistry.

A portrait of the late Prof. Morris Loeb was presented by Mrs. Loeb to New York University on Dec. 4th. The gift was accepted by Chancellor Brown on behalf of the University and memorial addresses were made by Professors Hill and Baskerville.

Prof. A. A. Noyes, of the Massachusetts Institute of Technology will give a course of lectures at the Throop College of Technology, Pasadena, Cal., during the second semester of the year.

Mr. Frank E. Carruth, a graduate of Wesleyan University, and a recent fellow in Cornell University, has been appointed assistant chemist in the North Carolina Experiment Station.

Mr. Richard K. Meade, Consulting Engineer, Baltimore, has been retained by the Louisville Portland Cement Co., to prepare plans for their new 60-ton per day hydrated lime plant. Mr. Meade is also directing the erection of a new steel and concrete stockhouse with self-emptying bins and a pack house equipped with Bates-Valve sacking machines for the Thomas Millen Co., Jamesville, N. Y.

Mr. R. A. Fetzner, a graduate of Davidson and Clemson Colleges, has been appointed instructor in chemistry in the North Carolina College of Agriculture and Mechanic Arts.

Mr. Ashmead G. Rodgers, General Superintendent of the

Carborundum Company's plant at Niagara Falls since 1902, died on Oct. 23, 1913, at the age of 41 years.

Prof. F. Haber, of Berlin, delivered the Hurter Memorial Lecture before the Liverpool Section of the Society of Chemical Industry, on Nov. 26, 1913. Subject: "Modern Chemical Industry."

Messrs. H. Solomon, D. E. Chadwick and L. S. Cunningham were recently appointed assistants in chemistry in the Mississippi Agricultural and Mechanical College, Agricultural College, Miss.

Dr. C. E. K. Mees, Director of the Eastman Kodak Company Research Laboratory, talked at a recent colloquium of the General Electric Company Research Laboratory, on Photographic Research.

The new chemical laboratory of the Mississippi Agricultural and Mechanical College is being occupied. The building is four stories high and contains about 40,000 sq. ft. of floor space; it is practically fireproof and provides commodious quarters for the state chemical work, as well as ample laboratories for regular college classes.

The International Oxygen Co. have removed their executive offices from 115 Broadway, New York City, to their works at Newark, N. J. Additional buildings have been erected to house the executive offices. The general sales offices will remain at 115 Broadway.

The Association of Official and Agricultural Chemists met in Washington, Nov. 17th-19th. The following officers were elected for the year: *Honorary President*—H. W. Wiley, Washington. *President*—E. F. Ladd, Fargo, N. D. *Vice-President*—C. H. Jones, Burlington, Vt. *Secretary*—C. L. Alsberg, Washington. *Additional Members of the Executive Committee*—J. D. Turner, Lexington, Ky.; W. F. Hand, Agricultural College, Miss.

Mr. C. J. Ramsburg, formerly Assistant Engineer of the United Gas Improvement Company of Philadelphia, is now 2nd Vice-President of the H. Koppers Company of Chicago.

Mr. M. D. Malcolmson has accepted a position in the Research Department of Thomas A. Edison at Orange, N. J.

Dr. W. D. Coolidge of the General Electric Company Research Laboratory has returned from a trip to Berlin in connection with the German patents on ductile tungsten.

The Chicago Section of the American Chemical Society has appointed the following committee to wait upon the Mayor of Chicago and offer their services, gratis, as an aid in the solution of all chemical problems relative to city waste: Prof. Harry McCormack, Professor of Chemistry, Armour Institute, *Chairman*; Mr. A. Lowenstein, Chief Chemist, Morris & Co.; Dr. J. H. Long, Professor of Chemistry, Northwestern University; Dr. Julius Stieglitz, Director of University Laboratories, Chicago University; Mr. William Brady, Chief Chemist, Illinois Steel Co.

## BOOK REVIEWS

**Mineral and Aerated Waters.** By C. AINSWORTH MYCHELL, B.A. (Oxon) F.I.C. 227 pages. Illustrated. New York, D. Van Nostrand Co. \$3.00.

This book, as stated in the preface, is intended to give an outline of the early methods of making artificial mineral waters and to trace the gradual evolution of the primitive forms of apparatus first invented into the carbonating plant of the present day.

Aside from the historical part there is little of interest to the chemist, with the exception of the chapters on carbon dioxide and radio-activity. The latter chapter (IV) is not only new but very instructive. The author gives tables showing the amount of helium, etc., in a number of the natural mineral waters, also an illustration and description of the apparatus for measuring the radio-activity of radium and other radio-active bodies, and for the preparation of artificial radio-active mineral waters.

Considerable space is devoted to washing and bottling machinery. The illustrations are good, but of little value to the American manufacturer as only English types are given.

The chapter on the Examination of Mineral Waters mentions the metallic contaminations, but with the exception of Arsenic gives no directions for detecting them. In regard to the Bacterioscopic examination and injurious Fermentations he gives considerable information. In this chapter we find rather a surprising statement in regard to the use of distilled water, *i. e.*, "It by no means follows that soda water prepared from it is any purer bacteriologically than that prepared from ordinary hard waters. In fact bacterioscopic examinations of soda water made from distilled water, have, in some cases given worse results than those obtained with soda water made from ordinary tap water." These conditions may exist in England but are not in accord with experiments made in this country.

In the preparation of Artificial Mineral Waters no idea is given of the methods in use at the present time.

The author makes a good suggestion in regard to the public advantage of enforcing precautions to prevent bacterial contamination, and to ensure the utmost cleanliness in the factory, and states that in any case, a system of inspection of factories

at irregular intervals would be a much more efficient safeguard of purity than even a frequent examination of samples bought at random.

The Bibliography is very complete, and should prove very useful to readers interested in this subject.

A. P. HALLOCK

**Technical Gas and Fuel Analysis.** By ALFRED H. WHITE. 276 pp. Price, \$2.00. McGraw-Hill Book Co., New York.

This book is a very complete treatise covering the subject fully and in a way that should be a great help to any chemist or engineer interested in the sampling and analysis of gases or fuels. The author has freely quoted from other works, and has pointed out the most accurate and practicable method of securing results of sufficient accuracy for all commercial work. He has summarized and discussed the work of committees of the various societies relative to calorimetry, photometry, coal analysis, etc. The author has laid particular stress upon the importance of sampling both gases and fuel and has pointed out many precautions that are too often overlooked. Several useful tables are included in the appendix.

E. G. BAILEY

**Die Verwendung der seltenen Erden.** By C. RICHARD BÖHM. 107 pp. 10 illustrations. Veit and Company, Leipzig, 1913.

This little handbook is a critical review in which this authority on the rare earths has brought together the more common as well as the unusual applications in the sciences and arts of these interesting elements.

The review is well done, and is as thorough as the literary work of the author invariably is.

The descriptions of the various uses of these earths should prove profitable reading to the chemist, and particularly to the research student.

No description is given of the use of the earths in the gas mantle, as that side is discussed by the author in a separate volume.

VICTOR LENHER



**Principles of Agricultural Chemistry.** By G. S. FRAPS, Ph.D. Easton, Pa., Chemical Publishing Company. London, Williams & Norgate. 1913. XXIV. 493 pp.

This book is based on lectures given for a number of years by the author to students in Agriculture. The work is devoted to the general chemical side of agriculture, and while some laboratory methods are given, it is in no sense intended for a laboratory manual devoted to analytical processes.

In the preface the author states that it is his aim "to present the fundamental principles of agricultural chemistry. The point of view is that of the chemist dealing with agricultural problems; the attempt is made to emphasize chemical methods of investigation, and inculcate scientific habits of thought. Details are omitted so far as they are not necessary to the proper treatment of the subject. Practical applications which are necessarily local, are left out as much as possible. The book thus treats of agricultural chemistry rather than of chemical agriculture. It attempts to give a comprehensive view of the subject, and to prepare the student for a more detailed study of its various phases."

The scope of the subject and the general importance of the relations of chemistry to agriculture are shown in the introduction which comprises the first chapter. Chapters II and III deal with the essentials of plant life, Chapter III treating more especially with the influence of the atmosphere; Chapters V, VI, VII, VIII, IX, X, XI, XII and XIII deal with soils; the next three chapters are devoted to fertilizers; Chapters XVII and XVIII to the composition and constituents of plants; Chapter XIX to digestion, and the remaining five chapters to the feeding of animals, utilization of food, calculation of rations, etc. Considerable space is devoted to experimental data and to proper methods of carrying on cultural experiments.

In the discussions of the different topics where different theories have been advanced by investigators of prominence, the author has noted the different views. The doctrines are sound and represent the latest ideas in scientific agriculture. It can hardly be considered a technical book, though it is somewhat too technical for the ordinary farmer; however, it contains a large amount of valuable information which would be useful in farm operations. It will be valuable in the class room and will be found interesting reading for all who are interested in Agricultural Chemistry.

On the whole, the book is an excellent one; the author has succeeded in presenting the facts relating to our present knowledge of agricultural chemistry in an intelligible and, generally, in an accurate manner.

The publishers have done their part well in producing a book of convenient size, printed on good paper with clear type, and altogether it forms an attractive volume both from the author's and publisher's standpoint.

F. B. CARPENTER

**Accident Prevention.** By JAS. B. DOUGLAS, Manager Claim Department, United Gas Improvement Company, Philadelphia. Published by the United Gas Improvement Company. 111 pp. Cloth bound.

This book includes a general statement in regard to the causes and prevention of accidents and is illustrated by a large number of photographs showing the features in and about a factory yard which have led to serious accidents, and the methods adopted for their prevention. It is an exceedingly valuable little book, and a careful consideration of the suggestions which it contains would reduce the number of accidents in almost any manufacturing plant.

M. C. WHITAKER

**Wissenschaftliche Grundlagen der Erölbearbeitung.** By DR. L. GURWITSCH. 278 pp. 16 figs. Julius Springer, Berlin. Price, \$2.50.

The author has successfully carried out his intention of giving to chemists interested in petroleum a book covering a general survey of the various scientific aspects of the industry. Practical questions of different processes and construction of factory apparatus have been purposely omitted.

The book is divided into three general parts. Part I (115 pp.) covers in detail the constitution of petroleum oils from the chemical and physical sides; the general characteristics of the oils found in Europe, America and Asia; and briefly the various hypotheses concerning the origin of these natural oils. Part II (130 pp.) gives very completely the theories of working the oils, under the divisions: Distillation, and Refining. Part III (27 pp.) is devoted to various products: benzine, burning oils, lubricating oils, paraffin, vaseline.

Although certain conclusions and statements of the author can be criticized—especially under the division "Distillation"—still the book is highly recommendable to oil chemists, and this collection of the scientific principles underlying the refining of petroleum should prove of considerable value. Generally speaking, the book is of a high class, the various curves and microphotographs being especially noteworthy.

ROBERT K. MURPHY

## NEW PUBLICATIONS

By D. D. BEROLZHEIMER, Librarian The Chemists' Club, New York

**Allen's Commercial Organic Analysis. Vol. VIII. Enzymes, Proteins, etc.** By W. D. DAVIS and SAMUEL S. SADDLER. 8 vols. 4th edition. 8vo. 696 pp. Price, \$5.00. P. Blakiston's Son & Co., Philadelphia.

**Analysis, Quantitative Chemical. Loose Leaf Laboratory Manual.** By CHARLES M. ALLEN. 1. 8vo. John Wiley & Sons, New York.

**Analysis, Technical Chemical. Loose Leaf Laboratory Manual.** By R. H. H. HUNGST. 1. 8vo. John Wiley & Sons, New York.

**Arsenic Compounds, Handbook of the Organic.** By A. BERTHEIM. 8vo. 94 pp. Price, \$2.00. Ferdinand Enke, Stuttgart. (German.)

**Assaying, Textbook of.** By C. BERINGER and J. J. BERINGER. 13th edition. 8vo. 476 pp. Price, \$4.00. Chas. Griffin & Co., London.

**Brass: The Approximate Melting Points of some Commercial Copper Alloys.** By H. W. GILLET and A. B. NORTON. 8vo. 9 pp. U. S. Bureau of Mines, Technical Paper 60.

**Catalysis in Organic Chemistry.** By PAUL SABATIER. 8vo. Price, \$2.50. Ch. Beranger, Paris. (French.)

**Chemistry, Exercises in General. Loose Leaf Laboratory Manual.** By CHARLES M. ALLEN. 1. 8vo. John Wiley & Sons, New York.

**Chemistry, Treatise on. Vol. II. The Metals.** By H. E. ROSCOE

AND C. SCHORLEMMER. New edition. 8vo. 1470 pp. Price, \$7.50. Macmillan Co., New York.

**Chlorophyll, Studies on.** By RICHARD WILLSTAETTER and ARTHUR STOLL. 8vo. 432 pp. Price, \$5.00. Julius Springer, Berlin. (German.)

**Coal Tar Distillation and Working up of Tar Products.** By ARTHUR R. WARNER. 8vo. 185 pp. Price, \$2.00. John Allan & Co., London.

**Dictionary of Applied Chemistry. Vol. V. Sodium-Z.** By EDWARD THORPE. 5 vols. Revised edition. 8vo. 830 pp. Price, \$13.50. Longmans, Green & Co., New York.

**Dyes and Dyeing.** By CHARLES E. FELLEW. 8vo. 272 pp. Price, \$2.75. Low, London. McBride, Nast & Co., New York.

**Dyes: Yearbook for Colorists and Dyers. XV.** By HERMAN A. METZ. Sm. 8vo. Price, \$4.19. Farbwerke-Hoechst Co., New York.

**Essential Oils: Semi-annual Report of Schimmel & Co. for October, 1913.** 8vo. 151 pp. Schimmel & Co., Miltitz-Leipzig.

**Fuel, An Introduction to the Study of.** By F. J. BRISLEE. 8vo. 269 pp. Price, \$2.25. Constable & Co., London.

**Inorganic Chemistry, Newer Views on.** By A. WERNER. 3rd edition. 8vo. 419 pp. Price, \$3.00. Friedrich Vieweg und Sohn, Brunswick. (German.)

- Materials, Laboratory Manual of Testing.** By WILLIAM K. HATT AND H. H. SCOFFIELD. 8vo. 138 pp. Price, \$1.25. McGraw-Hill Book Co., New York.
- Metals, The Alloy.** By ERNST PANCKE. 8vo. 82 pp. Price, \$1.25. Wilhelm Knapp, Halle. (German.)
- Mineral Industry, The. Its Statistics, Technology and Trade during 1912.** By CHARLES O. J. 8vo. 1090 pp. Price, \$10.00. McGraw-Hill Book Co., New York.
- Microchemistry, Textbook of.** By FRIEDRICH EMICH. 8vo. Price, \$1.75. J. F. Bergmann, Wiesbaden. (German.)
- Mortar Materials, Preparation of. Cement, Lime, Gypsum.** By KARL SCHUBERT. 4th edition. 8vo. 946 pp. Price, \$10.00. Ton-Industrie Zeitung, Berlin.
- Oils, Solvents, Gums, Waxes and Allied Substances.** By FREDERIC S. HYDE. 8vo. 182 pp. Price, \$2.00. D. Van Nostrand Co., New York.
- Sanitation, Handbook of.** By GEORGE M. PRICE. 1st edition. 12 mo. 350 pp. Price, \$1.50. John Wiley & Sons, New York.
- Silicates in Chemistry and Commerce.** By W. ASCH AND D. ASCH. 8vo. 456 pp. Price, \$5.25. Constable & Co., London. (Translation.)
- Sugar, White, Manufacture, Plantation.** By W. H. TH. HARLOFF AND H. SCHMIDT. 8vo. 150 pp. Price, \$2.50. Norman Rodger, London. (Translation in English.)
- Sugars and their Simple Derivatives.** By JOHN E. MACKENZIE. 8vo. Price, \$2.00. Gurney & Jackson, London.
- Textile Fibers, Chemical Technology of the.** By KARL STIRM. 8vo. 410 pp. Price, \$3.25. Gebrüder Borntraeger, Berlin. (German.)
- Water: Its Production, Use and Removal.** By FERDINAND FISCHER. 8vo. Price, \$4.00. Otto Spamer, Leipzig. (German.)
- Welding, Autogenous.** By L'INSTITUT SCIENTIFIQUE ET INDUSTRIEL. 8vo. 108 pp. Price, \$0.75. Mois Scientifique et Industriel, Paris. (French.)

## RECENT JOURNAL ARTICLES

- Alcohol, Manufacture of, from Wood Waste in the United States.** ANONYMOUS. *American Distillers' Review*, Vol. 3, 1913, No. 7, pp. 98-100.
- Alkali and Chlorine Compounds by Electrolysis, A New Diaphragm Process for the Manufacture of.** By J. B. C. KERSHAW. *Journal of the Society of Chemical Industry*, Vol. 32, 1913, No. 21, pp. 995-998.
- Alkali Processes, Electrolytic.** By J. B. C. KERSHAW. *Journal of the Society of Chemical Industry*, Vol. 32, 1913, No. 21, pp. 993-995.
- Alloys, Lead-Tin-Antimony and Tin-Antimony-Copper.** By WILLIAM CAMPBELL. *Proceedings of the 16th Annual Meeting of the American Society for Testing Materials*, Vol. 13, 1913, pp. 630-668.
- Analysis: Oils and Fats Used in Tanning.** By CHARLES B. OBERFELL. *Journal of the American Leather Chemists' Association*, Vol. 8, 1913, No. 12, pp. 496-504.
- Arsenic, The Iodometric Determination of, in Iron and Iron Ores after Precipitation with Phosphoric Acid.** By L. BRANDT. *Chemiker Zeitung*, Vol. 37, 1913, No. 141, pp. 1445-1447.
- Coal, Notes on the Carbonization of, in Vertical Retorts.** By O. B. EVANS. *American Gas Light Journal*, Vol. 99, 1913, No. 22, pp. 338-343 and 346-348.
- Coke, Characteristics of Basic.** By J. R. CAMPBELL. *Coal and Coke Operator*, Vol. 32, 1913, No. 6, pp. 89-91.
- Dyeing, A Contribution to the History of.** By JULIUS HUEBNER. *Journal of the Society of Chemical Industry*, Vol. 32, 1913, No. 22, pp. 1043-1051.
- Dyeing, Experiments in.** By A. W. DAVISON. *Journal of Physical Chemistry*, Vol. 17, 1913, No. 9, pp. 737-754.
- Elements, The Evolution of. (Radioactivity and Geology.)** By W. W. STRONG. *Radium*, Vol. 2, 1913, No. 2, pp. 24-27.
- Enameling or Coating Steel and Iron with Glass, The Art of.** By RAYMOND F. NAILLER. *Metallurgical and Chemical Engineering*, Vol. 11, 1913, No. 12, pp. 695-698.
- Evaporating Apparatus in Sugar Factories, The Effect of Air and other Incombustible Gases upon the Capacity of the Heating and.** By E. W. KERR. *Laosiana Planter and Sugar Manufacturer*, Vol. 51, 1913, No. 23, pp. 485-486.
- Extraction and Separation of Materials.** By BERTHOLD BLOCK. *Chemiker Zeitung*, Vol. 37, 1913, No. 139, pp. 1425-1428.
- Fuel: Gas versus Fuel Oil.** By HAROLD L. ALT. *American Gas Light Journal*, Vol. 99, 1913, No. 23, pp. 353-356.
- Fuels, Recent Progress in Sampling and Testing.** By JOHN B. C. KERSHAW. *Chemical World*, Vol. 3, 1913, No. 12, pp. 386-388.
- Fuel: The Use of Pulverized Coal in Metallurgical Furnaces.** By JAMES LORD. *Proceedings of the Engineers' Society of Western Pennsylvania*, Vol. 29, 1913, No. 7, pp. 363-417.
- Furnaces, Electric, Their Design, Characteristics and Commercial Application.** By WOLSEY MCA. JOHNSON AND GEORGE N. LIEBER. *Metallurgical and Chemical Engineering*, Vol. 11, 1913, No. 12, pp. 683-686.
- Furnace, The Iron Blast, and the Characteristics of its Fuels.** By J. E. JOHNSON, JR. *Metallurgical and Chemical Engineering*, Vol. 11, 1913, No. 12, pp. 687-693.
- Gas: Coal Lining.** By THOMAS HOLGATE. *American Gas Light Journal*, Vol. 99, 1913, No. 21, pp. 330-331.
- Glycerin, Analysis of Crude, by the International Standard Methods.** 1911. By R. G. CRIMWOOD. *Journal of the Society of Chemical Industry*, Vol. 32, 1913, No. 22, pp. 1039-1041.
- Hydrocellulose, Some Fatty Acid Esters of, and their Saponification.** By ALBERT STERN. *Zeitschrift fuer angewandte Chemie, Aufsatzteil*, Vol. 26, 1913, No. 91, pp. 673-677.
- Iron, The Influence of Silicon on the Solubility of Carbon in.** By G. CHARPY AND ANDRÉ CORNU. *Comptes rendus de l'Académie des Sciences*, Vol. 157, 1913, No. 20, pp. 901-903.
- Iron and Steel, Value of Existing Methods for the Determination of Oxygen in.** By W. R. FLEMING. *Proceedings of the 16th Annual Meeting of the American Society for Testing Materials*, Vol. 13, 1913, pp. 477-488.
- Oil, Testing of Chinese Wood.** By E. W. BOUGHTON. *Proceedings of the 16th Annual Meeting of the American Society for Testing Materials*, Vol. 13, 1913, pp. 923-946.
- Paper, Clays Used for Coating and Loading.** By ALEXANDER R. VORABERGER. *Paper*, Vol. 13, 1913, No. 13, pp. 15-18.
- Paper: Removing Water of Condensation from Dryers.** By E. H. FRITCHMAN. *Paper*, Vol. 13, 1913, No. 11, pp. 15-18 and 34.
- Refractories, Testing of.** By A. V. BLINKINGER. *Proceedings of the 16th Annual Meeting of the American Society for Testing Materials*, Vol. 13, 1913, pp. 967-982.
- Rubber, Coloring, with Organic Coloring Matters.** By DITMAR. *India Rubber Journal*, Vol. 46, 1913, No. 21, pp. 1057-1058.
- Rubber: The Role of Polypropylene Sulfide in Vulcanization.** By H. SPELLO. *India Rubber Journal*, Vol. 46, 1913, No. 16, pp. 723-724.
- Shellac Bleaching.** ANONYMOUS. *Drugs, Oils and Paints*, Vol. 29, 1913, No. 6, pp. 209-212.
- Sizing, The Use of Talc for.** By H. ROSENBERG. *Canadian Textile Journal*, Vol. 30, 1913, No. 12, pp. 373-374.
- Steam, Generation of.** By CHARLES L. HUBBARD. *Steam*, Vol. 12, 1913, No. 8, pp. 153-155.
- Wood Cellulose.** By ARTHUR KLEIN. *Zeitschrift fuer angewandte Chemie, Aufsatzteil*, Vol. 26, 1913, No. 93, pp. 692-694.
- Wood Distillation.** By OSSIAN ASCHAN. *Zeitschrift fuer angewandte Chemie, Aufsatzteil*, Vol. 26, 1913, No. 95, pp. 709-713.
- Wood, Impregnation with Fluorids, Practical Results of.** By ROBERT NOWOTNY. *Zeitschrift fuer angewandte Chemie, Aufsatzteil*, Vol. 26, 1913, No. 93, pp. 694-700.

## RECENT INVENTIONS

By C. L. PARKER, Solicitor of Chemical Patents, McGill Building, Washington, D. C.

**Making Lactic Acid.** O. Friedberger, Oct. 7, 1913. U. S. Pat. 1,074,708. Lactic acid is produced by fermenting a saccharid by the *Bacillus Delbrücki*, previously brought to a healthy development and accustomed to dextrose.

**Converting Phosphorites.** H. V. Dunham, Oct. 7, 1913. U. S. Pat. 1,074,779. The phosphoric acid of phosphate rock is converted into the ammonium citrate-soluble state, but not into the water-soluble state, by heating an intimate mixture of the rock, a carbonate and a sulfate to a white heat in the absence of reducing agents, for about an hour.

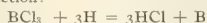
**Fertilizer.** A. R. Frank, Oct. 7, 1913. U. S. Pat. 1,074,785. The composition contains a cyanamid salt, free lime and an acid sulfate adopted to neutralize a portion of the lime.

**Fertilizer.** Newberry and Barrett, Oct. 7, 1913. U. S. Pat. 1,074,808. An intimate mixture of insoluble phosphate and an amount of gypsum and carbonaceous matter each approximately equal to two-thirds of the phosphoric acid contained in the phosphate, are calcined and ground.

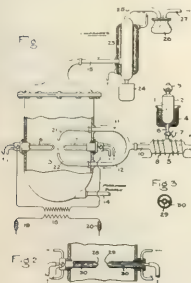
**Promoting Fermentation.** E. Pohl, Oct. 7, 1913. U. S. Pat. 1,074,814. Malt is produced in the presence of water

containing zeolites, mashed to form wort in the presence of the zeolites and fermented, still in the presence of the zeolites.

**Metalloidal Materials.** E. Weintraub, Oct. 7, 1913. U. S. Pat. 1,074,672. Elemental boron differing materially from the material commonly designated as boron in the technical literature, is produced by passing boron chlorid vapor and hydrogen through an electrical arc, the boron being produced according to the following reaction:



The boron is described as being a dense, hard, black mass having a high melting point, convertible by oxidation into boric anhydrid, being electrically conductive and having a very high negative temperature resistance coefficient, its conductivity approximately doubling for  $17^\circ\text{C}$ . rise in temperature above room temperature. The material can be fused into dense bodies having a conchoidal fracture and a hardness considerably greater than sapphire (see THIS JOURNAL, 5, 106).



**Electrolysis.** H. M. DuBois, Oct. 7, 1913. U. S. Pat. 1,075,026. The process consists in flowing the electrolyte over the upper end of a vertically arranged diaphragm and thence downward between the diaphragm and the exposed cathode surface, whereby the flowing of the cathode liquor is not dependent solely upon the porosity of the diaphragm, while the electrolyte action is unimpaired.

**White Lead.** E. Euston, Oct. 7, 1913. U. S. Pat. 1,075,143. Basic carbonate of lead is first precipitated by carbon dioxide from basic lead acetate solution maintained alkaline. A precipitate is then separately formed by the action of carbon dioxide upon basic lead acetate solution eventually acid and the two precipitates are mixed in proportions to form a pigment containing 11.3 per cent to 14.5 per cent carbon dioxide.

**Refining and Purifying Oils.** D. F. Lasher, Oct. 14, 1913. U. S. Pat. 1,075,481. Petroleum is treated with acid and alkali, washed to remove these materials and run through rice hull ashes.

**Arc Lamp Electrode.** G. M. Little, Oct. 14, 1913. U. S. Pat. 1,075,484. The electrode contains iron oxid and potassium silicate.

**Treating Cream and Similar Substances.** F. H. Stanley, Oct. 14, 1913. U. S. Pat. 1,075,514. The material under treatment is inoculated with lactic acid germs and impregnated with oxygen in the form of air, during the development of the lactic acid germs.

**Metal Filaments.** C. A. Hansen, Oct. 14, 1913. U. S. Pat. 1,075,563. A squirtable mixture for the manufacture of lamp filaments is produced comprising an oxid of tungsten starch, glucose and glycerin.

**Anhydrid of Salicylic Acid.** Kopetschni, Karczag and Fodor, Oct. 14, 1913. U. S. Pat. 1,075,581. Salicylic acid chlorid is treated to split off therefrom hydrochloric acid. The resulting anhydrid of salicylic acid is described as being readily

soluble in ether, acetone, glacial acetic acid, ethyl acetate and benzol, melting between  $90^\circ$  and  $100^\circ\text{C}$ . and converted by boiling with anilin into salicylanilid.

**Molten Bath and Means for Coating Iron Articles Therewith.** H. J. Lohmann, Oct. 14, 1913. U. S. Pat. 1,075,583. A coating bath of molten lead and zinc is maintained in a homogeneous condition for an indefinite length of time by the addition of a small proportion of mercury.

**Ferrosoferric Oxid.** H. Goldschmidt, Oct. 14, 1913. U. S. Pat. 1,075,709. Mill scale is calcined by an oxidizing flame and impurities removed by magnetic separation, the product being mixed with a powdered reducing metal.

**Waste Sulfite Liquor.** H. H. Hurt, Oct. 14, 1913. U. S. Pat. 1,075,916. A tanning composition is produced by treating waste sulfite liquor containing the original organic matters in their unchanged normal relative ratios, with a sesquioxid salt of an acid capable of forming insoluble lime salts and removing the insoluble lime salts produced.

**Translucent Uniformly-Colored Paraffin.** J. v. R. v. Alkamede, Oct. 14, 1913. U. S. Pat. 1,076,000. Paraffin is rendered uniformly translucent by removing the air from it and excluding the air until the material has cooled to molding condition.

**Precious-Metal-Dissolving Means.** H. Foersterling, Oct. 14, 1913. U. S. Pat. 1,076,006. A homogeneous solidified mixture of sodium cyanid and sodium bromid is formed and dissolved in the presence of an oxidizing agent, such as an acid solution of hydrogen peroxid.

**Converting Phosphorites.** H. V. Dunham, Oct. 21, 1913. U. S. Pat. 1,076,200. An intimate mixture of phosphate rock, an alkali metal salt in amount sufficient to convert the phosphate into citrate-soluble but not water-soluble condition, and a sufficient amount of alumina to prevent fusion is heated to a white heat.

**Water-Resistant Cement.** C. Ellis, Oct. 21, 1913. U. S. Pat. 1,076,028. The cement is produced by passing finely-divided dry mineral material capable of bonding on exposure through an atomized spray of a normally-solid organic waterproofing material maintained in molten condition.

**Peroxid of Hydrogen.** C. R. Jacobs, Oct. 21, 1913. U. S. Pat. 1,076,039. The compound consists of anhydrous metaborate of sodium peroxid which upon the addition of water produces a non-acid and non-caustic solution of peroxid of hydrogen.

**Separating Phosphoric Acid from Natural Phosphates.** M. M. Haff, Oct. 21, 1913. U. S. Pat. 1,076,497. Sixty parts of a non-feldspathic aluminum silicate and one hundred parts of a natural phosphate are subjected to the heat of an electric arc to volatilize the phosphoric acid, which is condensed.

**Separation of Lead from Zinc.** J. Babé, Sept. 16, 1913. U. S. Pat. 1,073,461. The mixture to be separated is heated to from  $800^\circ$  to  $900^\circ\text{C}$ . in the presence of a mixture of alkaline sulfid and carbon powder impregnated with sulfuric acid whereby the lead is sulfuretted while the zinc is unaffected.

**Substitute for Rubber.** J. B. Scammell, Sept. 16, 1913. U. S. Pat. 1,073,527. Cotton is first soaked in butyric acid, the excess of acid being removed. The treated cotton is then added to an oil vulcanizable by sulfur chlorid. Sulfur chlorid is added to dissolve the cotton and the acids formed are neutralized. A further quantity of sulfur chlorid is then added to cause the mixture to solidify.



# MARKET REPORT

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR THE MONTH OF DECEMBER, 1913

## ORGANIC CHEMICALS

Acetanilid.	Lb.	21	@	23
Acetic Acid (28 per cent).....	C.	1.75	@	1.90
Acetone (drums).....	Lb.	13 1/4	@	14 1/4
Alcohol, denatured (180 proof).....	Gal.	33	@	36
Alcohol, grain (188 proof).....	Gal.	2.48	@	2.50
Alcohol, wood (95 per cent).....	Gal.	46	@	48
Amyl Acetate.....	Gal.	1.90	@	2.00
Aniline Oil.....	Lb.	10	@	10 1/2
Benzoic Acid.....	Lb.	23	@	27
Benzol (90 per cent).....	Gal.	21	@	23
Camphor (refined in bulk).....	Lb.	42 1/4	@	44
Carbolic Acid (drums).....	Lb.	8	@	10
Carbon Bisulfide.....	Lb.	6 1/4	@	8
Carbon Tetrachloride (drums).....	Lb.	7 3/4	@	7 1/2
Chloroform.....	Lb.	25	@	35
Citric Acid (domestic), crystals.....	Lb.	51	@	52
Dextrine (corn).....	C.	2.92	@	3.13
Dextrine (imported potato).....	Lb.	6	@	7
Ether (U. S. P., 1900).....	Lb.	14	@	20
Formaldehyde.....	Lb.	8 1/4	@	9 1/4
Glycerine (dynamite).....	Lb.	19 1/4	@	20
Oxalic Acid.....	Lb.	7 1/4	@	7 1/2
Pyrogallie Acid (bulk).....	Lb.	1.20	@	1.40
Salicylic Acid.....	Lb.	25	@	30
Starch (cassava).....	Lb.	3 1/4	@	4
Starch (corn).....	C.	2.24	@	2.90
Starch (potato).....	Lb.	4 1/4	@	5
Starch (rice).....	Lb.	8	@	9
Starch (sago).....	Lb.	2 1/4	@	2 1/4
Starch (wheat).....	Lb.	5 1/4	@	6 1/4
Tannic Acid (commercial).....	Lb.	35	@	36
Tartaric Acid, crystals.....	Lb.	31 1/4	@	31 1/4

## INORGANIC CHEMICALS

Acetate of Lead (brown, broken).....	Lb.	7 3/4	@	8
Acetate of Lime (gray).....	C.	2.00	@	2.05
Alum (lump).....	C.	1.75	@	2.00
Aluminum Sulfate (high-grade).....	C.	1.25	@	1.75
Ammonium Carbonate, domestic.....	Lb.	8	@	8 1/2
Ammonium Chloride, gray.....	Lb.	5 1/4	@	6 1/4
Aqua Ammonia (drums) 16°.....	Lb.	2 1/4	@	2 1/4
Arsenic, white.....	Lb.	3	@	4
Barium Chloride.....	Lb.	1.60	@	1.75
Barium Nitrate.....	Lb.	5 1/4	@	5 1/2
Barytes (prime white, foreign).....	Ton	19.00	@	23.50
Bleaching Powder (35 per cent).....	C.	1.22 1/2	@	1.30
Blue Vitriol.....	Lb.	5	@	5 1/4
Borax, crystals (bags).....	Lb.	3 3/4	@	4 1/4
Boric Acid, crystals (powd.).....	Lb.	7	@	7 1/2
Brimstone (crude, domestic).....	Ton	22.00	@	22.50
Bromine, bulk.....	Lb.	30	@	35
Calcium Chloride, fused.....	C.	60	@	90
Chalk (light precipitated).....	Lb.	4	@	4 1/2
China Clay (imported).....	Ton	nominal		
Feldspar.....	Ton	8.00	@	12.00
Fuller's Earth, powdered, Foreign.....	Ton	16.00	@	17.00
Green Vitriol (bulk).....	C.	55	@	60
Hydrochloric Acid (18°).....	C.	1.15	@	1.55
Iodine (resublimed).....	Lb.	3.55	@	3.60
Lead Nitrate.....	Lb.	7 3/4	@	8 1/4
Litharge (American).....	Lb.	3 1/2	@	5 1/4
Lithium Carbonate.....	Lb.	65	@	70
Magnesium Carbonate.....	Lb.	21	@	35
Magnesite "Calced".....	Ton	28.50	@	29.50
Nitric Acid, 36°.....	Lb.	3 1/4	@	4 1/4
Phosphoric Acid (sp. gr. 1.75).....	Lb.	21 1/2	@	25 1/4
Phosphorus.....	Lb.	45	@	1.00
Plaster of Paris.....	Bbl.	1.50	@	1.70
Potassium Bichromate, 50°.....	Lb.	6 3/4	@	7
Potassium Bromide.....	Lb.	39	@	40
Potassium Carbonate (calced), 80 @ 85%.....	C.	3.25	@	3.30
Potassium Chlorate, crystals.....	Lb.	7 1/4	@	7 1/2
Potassium Cyanide (bulk), 98-99%.....	Lb.	16	@	18
Potassium Hydroxide.....	C.	4.00	@	4.25
Potassium Iodide (crude).....	Lb.	2.95	@	3.00
Potassium Nitrate (bulk).....	Lb.	4 1/4	@	5
Potassium Permanganate (bulk).....	Lb.	8 1/4	@	10
Quicksilver, Flask (75 lbs.).....	39.00	@	40.00	
Red Lead (American).....	Lb.	6	@	6 1/4
Salt Cake (glass-makers').....	C.	55	@	65

Silver Nitrate.....	Oz.	36 1/4	@	35 1/2
Soapstone in bags.....	Ton	10.00	@	12.00
Soda Ash (48 per cent).....	C.	6 1/4	@	7 1/4
Sodium Acetate.....	Lb.	3 1/4	@	4 1/4
Sodium Bicarbonate (domestic).....	C.	1.00	@	1.10
Sodium Bicarbonate (English).....	Lb.	2 1/4	@	3
Sodium Bichromate.....	Lb.	4 1/4	@	5 1/4
Sodium Carbonate (dry).....	C.	60	@	80
Sodium Chlorate.....	Lb.	7 1/4	@	7 1/2
Sodium Hydroxide, 60 per cent.....	C.	1.55	@	1.57 1/2
Sodium Hyposulfite.....	C.	1.30	@	1.60
Sodium Nitrate, 95 per cent, spot.....	C.	1.30	@	2.20
Sodium Silicate (liquid).....	C.	65	@	1.50
Strontium Nitrate.....	Lb.	6 1/4	@	7
Sulfur, Flowers (sublimed).....	C.	2.20	@	2.60
Sulfur, Roll.....	C.	1.85	@	2.15
Sulfuric Acid, 60° B.....	C.	85	@	1.00
Talc (American).....	Ton	15.00	@	20.00
Terra Alba (American), No. 1.....	C.	75	@	80
Tin Bichloride (50°).....	Lb.	12 1/4	@	13 1/2
Tin Oxide.....	Lb.	42	@	44
White Lead (American, dry).....	Lb.	5 1/4	@	5 1/2
Zinc Carbonate.....	Lb.	8 1/4	@	9
Zinc Chloride (granulated).....	Lb.	4 1/4	@	5
Zinc Oxide (American process).....	Lb.	5 1/4	@	6 1/4
Zinc Sulfate.....	Lb.	2 1/4	@	3

## OILS, WAXES, ETC.

Beeswax (pure white).....	Lb.	44	@	46
Black Mineral Oil, 29 gravity.....	Gal.	13 1/4	@	14
Castor Oil (No. 3).....	Lb.	8 1/4	@	8 1/2
Ceresin (yellow).....	Lb.	12	@	22
Corn Oil.....	C.	6.80	@	6.85
Cottonseed Oil (crude), f. o. b. mill.....	Gal.	40	@	41
Cottonseed Oil (p. s. y.).....	Lb.	6.70	@	6.75
Cylinder Oil (light, filtered).....	Gal.	21 1/4	@	32
Japan Wax.....	Lb.	10 1/4	@	10 3/4
Lard Oil (prime winter).....	Gal.	92	@	94
Linseed Oil (raw).....	Gal.	48	@	49
Menhaden Oil (crude).....	Gal.	33	@	37
Neatsfoot Oil (20°).....	Gal.	96	@	98
Paraffine (crude, 120 & 122 m. p.).....	Lb.	3 1/4	@	3 1/4
Paraffine Oil (high viscosity).....	Lb.	26	@	28
Rosin ("P" grade) (280 lbs.).....	Bbl.	4.15	@	4.30
Rosin Oil (first run).....	Gal.	27	@	28
Shellac, T. N.....	Lb.	19 1/4	@	21
Spermaceiti (caked).....	Lb.	30	@	35
Sperm Oil (bleached winter), 38°.....	Gal.	72	@	74
Spindle Oil, No. 200.....	Gal.	18	@	19
Stearic Acid (double-pressed).....	Lb.	9	@	12
Tallow (acidless).....	Gal.	65	@	66
Tar Oil (distilled).....	Gal.	30	@	31
Turpentine (spirits of).....	Gal.	45 1/4	@	46

## METALS

Aluminum (No. 1 ingots).....	Lb.	18 1/4	@	18 3/4
Antimony (Hallet's).....	Lb.	7	@	7 1/2
Bismuth (New York).....	Lb.	2.05	@	2.10
Bronze powder.....	Lb.	50	@	3.00
Copper (electrolytic).....	Lb.	14 1/4	@	14 1/2
Copper (lake).....	Lb.	14 1/4	@	14 1/2
Lead, N. Y.....	Lb.	3.85	@	—
Nickel.....	Lb.	50	@	55
Platinum (refined).....	Oz.	43.50	@	44.50
Silver.....	Oz.	57 1/4	@	58
Tin.....	C.	37.40	@	37.80
Zinc.....	C.	5.15	@	5.20

## FERTILIZER MATERIALS

Ammonium Sulfate.....	C.	2.95	@	3.00
Blood, dried.....	Unit	3.30	@	—
Bone, 4 1/2 and 50, ground, raw.....	Ton	27.25	@	28.00
Calcium Nitrate (Norwegian).....	C.	2.05	@	2.10
Castor meal.....	Unit	nominal		
Fish Scrap, domestic, dried.....	Unit	nominal		
Mowrah meal.....	Unit	nominal		
Phosphate acid, 16 per cent bulk.....	Ton	—	@	7.00
Phosphate rock; f. o. b. mine.....	Ton	2.75	@	3.00
Florida land pebble, 68 per cent.....	Ton	5.00	@	5.50
Tennessee, 70-80 per cent.....	Ton	39.07	@	—
Potassium, "muriate," basis 80 per cent.....	Ton	0.13 1/4	@	—
Pyrites, furnace size, imported.....	Unit	3.25	@	10
Tankage, high-grade.....	Unit	3.25	@	10

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## TABLE OF CONTENTS

### EDITORIALS:

The Invention of Celluloid.....	90
ORIGINAL PAPERS:	
The Composition of Paint Vapors. By Henry A. Gardner.....	91
Metallography as Applied to Inspection. By Wirt Tassin.....	95
Mahone Petroleum. By Charles F. Mabery.....	101
The Preparation of Metallic Cobalt by Reduction of the Oxide. By Herbert T. Kalmus.....	107
Oxides of Cobalt. By Herbert T. Kalmus.....	115
The Analytical Constants of Hydrogenated Oils. By Carleton Ellis.....	117
The Chemistry and Properties of Glycerophosphates (Glycerinophosphates). By Gaston DuBois.....	122
Toxicity of Various Wood Preservatives. By C. J. Humphrey and Ruth M. Fleming.....	128
A Rapid Method for Determining the Percentage of Casein in Milk. By W. O. Walker.....	131
I. A New Electrically Controlled and Timed Asphalt Penetrometer. II. The Effect of Penetrations of Variations in Standard Needles. By Hermann W. Mahr.....	133
An Apparatus and Method for Determining the Hardness of Butterfat. By A. E. Perkins.....	136
Influence of Small Amounts of Ethyl Alcohol on Fermentation in Cane Sugar Syrup. By C. B. Cochran and J. H. Perkins.....	141

### LABORATORY AND PLANT:

Filter Presses. By E. J. Sweetland.....	142
Improvised Mine Fires on an Experimental Scale.....	146
A Shaker for the Mechanical Analysis of Soil. By Freeman Ward.....	147

### ADDRESSES:

The Present Status of the Wood Turpentine Industry. By E. H. French and James R. Withrow.....	148
Chemistry as Affecting the Profitableness of Industry. By G. W. Thompson.....	152

### PERKIN MEDAL AWARD:

Chairman's Address. By Gustave W. Thompson.....	155
Presentation Address. By Charles F. Chandler.....	156
Address of Acceptance. By John Wesley Hyatt.....	158
Personal Reminiscences. By Frank Vanderpoel.....	161

### CURRENT INDUSTRIAL NEWS:

Evaluation of Pulp Wood.....	163
Progress in the Fixation of Nitrogen in Scandinavia.....	163
Standard Specifications for the Purity of Raw Linseed Oil from North American Seed.....	164
Uranium, Radium and Vanadium Report.....	164
The Approximate Melting Point of Some Commercial Copper Alloys.....	164
Bureau of Mines Budget.....	165
Platinum Deposits in Germany.....	165
U. S. Mineral Production, 1912.....	165
Oil-Hardening Plant in Norway.....	165
Concentrated Nitric Acid in Norway.....	165
Proposed Beet-Sugar Factory for Chile.....	166
Production of Portland Cement in 1913.....	166
Natural Gaseous Mixtures Rich in Helium.....	166

### NOTES AND CORRESPONDENCE:

Purification of Water by Adsorption. Preliminary Announcement.....	166
Note on Certain Unpublished Work on Electrolysis Using Supported Mercury Cathode.....	166
Synthetic Resins.....	167
Ozone.....	170
Rapid Determination of Copper in Steel, Cast Iron and Alloy Steels.....	170
International Electrical Congress, 1915.....	171
Spring Meeting of the American Chemical Society.....	171
Bureau of Standards' Analyzed Samples.....	171
Synthetic Resins—Correction.....	171
Vegetable Oils Exported from China, 1912.....	171
Annual Tables of Constants, Etc., Vol. III.....	171

### PERSONAL NOTES.....

### BOOK REVIEWS:

Dictionary of Applied Chemistry; Transactions of the American Institute of Chemical Engineers; General Metallurgy; Plantation White Sugar Manufacture; Metallurgical Analysis; Review of the Examination of Water and Water Supplies; Chemical Technology and Analysis of Oils, Fats and Waxes.....	173
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### NEW PUBLICATIONS.....

### RECENT INVENTIONS.....

### MARKET REPORT.....

## EDITORIALS

### THE INVENTION OF CELLULOID.<sup>1</sup>

Never has the Perkin Medal been better awarded than to John Wesley Hyatt. He created a distinctly American industry, chemical in its very essence, although the inventor never claimed to be a chemist. He not only invented the fundamental principle on which this important industry is based, but he gave his fertile inventive genius and the better part of his life to the development of the many details which built up the technique of celluloid.

The technique of celluloid is strikingly different from that of rubber and all other plastics. This explains why rubber technologists ordinarily fail when they attempt celluloid manufacturing. It provides an excuse why the hard rubber concerns of this country failed to see the coming importance of celluloid when the new material was offered to them.

I believe it was Rudyard Kipling who, in one of his writings, refers to a fisherman who was specially successful because "he could think as a cod-fish would think." I have observed in meeting celluloid or rubber manufacturers that the former cannot think but "celluloid," and the latter "rubber," and are much at sea when they are confronted with the technique of a new plastic.

The history of the discovery and industrial development of celluloid by Hyatt has been described in detail by E. C. Worden, in "The Nitrocellulose Industry," Van Nostrand, New York, 1911.

I may mention here, from conversations with the inventor himself, that celluloid and the celluloid industry with all that it implies, after all meant merely a big parenthesis in the life of Hyatt in his quest of a perfect billiard ball which would replace the expensive ivory article. This is so true that even during his later years, when he is well in the seventies, he has spent considerable time in the study of other plastics in his effort to still further perfect billiard balls. Celluloid and the celluloid industry are by no means the only inventions which Hyatt has to his credit; the famous Hyatt Roller Bearing which has developed into a large and successful manufacturing enterprise, his methods of water purification (with Isaiah S. Hyatt), his process for crushing sugar cane, and his many other patents testify to the abundance as well as the diversity of his inventive achievements.

The invention of celluloid is an excellent example of how sometimes it is a real advantage for a man of genius not "to know too much;" not to be hampered by too much book knowledge if the latter tends to petrify the mind into a too one-sided point of view. In all his work Hyatt's keen observing mind was his sole guide. He tried things for himself. He did not rely overmuch on what others told him to be the facts, or on what was written in books. He wanted to be his own "authority." He had found by ex-

perience that there are many things printed in books and chemical treatises "that ain't so."

He thus discovered the important fact, on which the whole celluloid industry is based, that a mixture of nitrocellulose, camphor and a small amount of alcohol, when properly prepared, becomes thermoplastic. In other words, it becomes soft when heated, can be molded in a hydraulic press, and after cooling to ordinary atmospheric pressure, it becomes again hard and strong.

His predecessors all used nitrocellulose in presence of relatively large amounts of solvents, and used a solution, or a relatively soft mass, from which the solvents were left to evaporate. This not only meant a considerable loss of solvents, but restricted enormously many possible technical applications. The mass shrunk in the act of drying, and rapid molding was impractical, if not totally impossible.

Some of his predecessors had even used camphor in their solutions, although Hyatt knew nothing about this until it came out later in his patent suits. But his predecessors had used camphor merely as any other solvent. They had failed to observe or to grasp the great technical importance of the fact that camphor could make a solid solution with nitrocellulose and produce a thermoplastic mass.

This seemingly simple observation might have left very little imprint on any other but the actively constructive mind of a Hyatt. He saw right away that from that moment on, he could employ purely mechanical means for molding rapidly and effectively, and develop the technique of nitrocellulose plastics, for purposes never dreamt of before. The principle was simple and the available methods seemed simple enough. But as usual, when one tries a process commercially, it was found that there were endless details which conspired to render the industrial and commercial development a far more difficult problem than the mere discovery of the new principle in the laboratory. Here the whole problem might have suffered shipwreck in the hands of any other man than Hyatt. The whole technique of celluloid was then developed painstakingly by him, in all its endless details. Special machinery was invented, new methods were conceived. All this is shown by the numerous subsequent Hyatt patents.

It is an axiom that the test of a valuable invention is that it should be infringed, or attacked by those whose thinking cells are passive until some inventor arouses them out of their mental drowsiness.

Hyatt, in his patent suits, had plenty of experience of the kind. Fortunately, his financial backers could afford to defend his rights in the absurdly long and expensive patent litigation, which is a proverbial characteristic of the inefficient administration of the patent laws of this country.

I believe it was George Westinghouse who reminded us that every successful invention passes through three

<sup>1</sup> The Perkin Medal for valuable researches leading to the establishment of industries was awarded on January 23rd to Mr. Hyatt. A full report of the meeting is published in this issue of THIS JOURNAL.



stages: The *first*, when it is said: "Such a thing is absurd or impossible." The *second* stage, after the patent descriptions have become public, and have given others the means to imitate and try to find loopholes in the patent claims, begins when it is said: "The thing is not new." And *finally*, after the usefulness of the invention has become so obvious and the details connected therewith have penetrated through the hard skulls of the laggards, then it sounds: "There is no invention at all."

Lawyers are great in this game. Hyatt's invention went through every one of these three stages and were it not for the Perkin Medal, many of us might have forgotten that there ever was such a man as Hyatt, and that there was a time when celluloid did not exist, or involved very difficult problems.

His patents were assailed on the ground that others before him had used solvents and camphor in conjunction with nitrocellulose, but it was studiously omitted that his predecessors had used these ingredients under entirely different conditions, for entirely different purposes, and could not produce in that way, Hyatt's valuable technical effect. The very solvents which proved a bar to any important applications for molded plastics, Hyatt did away with, when he conceived his thermoplastic mass.

Some of the early drawbacks in the technical applications of Hyatt's discovery were none other than chemical experts with which his financial backers surrounded him. Hyatt knew no chemistry, but he knew well observed facts intimately connected with the details of the work he had undertaken. His knowledge of nitrocellulose was obtained piece-meal by his own experimenting. Facts found in books he accepted only after he had verified them. It so happened that he frequently noticed that printed statements did not agree with his own observations. One of the chemical experts insisted that "cellulose was cellulose," regardless of the source of supply, provided it was sufficiently purified, and that nitrocellulose made from any kind of pure cellulose had the same properties. Hyatt knew better when he found that the article

made from ramie, the strongest and most expensive cellulose, was incomparably superior to that obtained from cheap cotton or cheap pulp cellulose.

Some chemical experts also made the positive statement to his backers, that his process would surely lead to terrific explosion because he was heating in a hot press nothing less than guncotton, which was known to be a violent explosive. Though Hyatt stated that he had been using his process for quite a time and still was alive, it was objected that this was simply due to sheer good luck which would cease at some time; if ever it happened that by accident or carelessness, the heat in his presses rose a little higher, a violent explosion was bound to occur, and this would be the end of the celluloid industry. These arguments were not by any means without logic. At that time, it is doubtful whether any chemist who knew the chemical properties of nitrocellulose would not have thought it the height of folly to heat this substance under pressure.

Hyatt not being a chemist, preferred to try and see for himself what would occur. He took a good-sized block of celluloid and heated it in the hydraulic press at a temperature far superior to the relatively low temperatures he was using in practice. He tells me that he was sufficiently impressed by all the threatening talk of the chemical experts to screen himself from the press by means of several thicknesses of cross boards behind which he could peep on and see what was going to occur. After the temperature rose to the point when the celluloid began to be destroyed, the block started sizzling on account of the emission of gaseous products. But he continued the experiment until he made sure that nothing worse occurred than to spoil the material.

The pessimistic chemical experts had failed to take into consideration that the introduction of such a large proportion of camphor had profoundly modified the properties of nitrocellulose. They had also overlooked the fact that soluble nitrocellulose is not nitrated so much as the more explosive higher nitrated cotton.

L. H. BAEKELAND

## ORIGINAL PAPERS

### THE COMPOSITION OF PAINT VAPORS

By HENRY A. GARDNER<sup>1</sup>

Received December 18, 1913

Freshly painted surfaces give to the surrounding air a peculiar odor. In closed rooms, this odor is pronounced. Its nauseating effects are well known. Painters are in the habit of stating that the vapors of fresh paint have a "leady smell." This is probably due to the fact that white lead is used as the base upon which the majority of paints are prepared. The painter has therefore always associated this pigment with the characteristic odor of fresh paint. Some cases of illness among painters have been ascribed to the effects of paint vapors. People occupying freshly decorated sleeping rooms which are not well ventilated, have at

times complained of illness from the same cause. E. C. Baly<sup>1</sup> examined spectroscopically the vapors from basic carbonate-white lead paint, and found evidences of metallic lead therein. The vapors from basic sulfate-white lead paint or zinc oxide paint, when examined in a similar manner, showed the absence of metallic constituents. Some cases of lead poisoning among painters could be ascribed to the vapors from basic carbonate-white lead paints, if lead compounds could actually be found present in such vapors. Armstrong and Klein,<sup>2</sup> after conducting an elaborate series of tests, concluded that lead is not present in the vapors from white lead paint, but that the toxic effects produced by such vapors are due almost entirely to the volatile substances given off by the turpentine present.

<sup>1</sup> Assistant Director, The Institute of Industrial Research, Washington, D. C.

<sup>2</sup> *The Oil and Colour Trades Journal*, May 6, 1911, p. 1518.

<sup>3</sup> *J. S. C. I.*, **32**, 320 (1913).

The writer has made a series of tests which confirm those of Armstrong and Klein, insofar as their results are concerned with the non-metallic constitution of paint vapors. The writer's tests, however, show that the vapors from paint apparently contain carbon monoxide, the poisonous nature of which is too well known to be commented upon. The amount of carbon monoxide evolved is also shown to be directly influenced by the type of pigments used in the paint. The definite presence of aldehydes and organic acid substances in paint vapors has also been established by these tests. The data presented has brought forth considerable information regarding the phenomenon of oxidation as applied to linseed oil and linseed oil paints. The results are given with a view to awakening further research work of a similar nature. An outline of the tests made is herewith presented, together with a summary of the results obtained and in some instances a discussion of the data. Many of the tests outlined were made in duplicate.

**EXPERIMENT I.**—Four cylinders each 30 in. long and 9 in. in diameter, were formed of galvanized sheet iron. One end of each cylinder was fitted with a removable lid. The other end was closed. The seams were all soldered. The tanks were numbered from 1 to 4. The interiors of the tanks were brush-coated with raw linseed oil, soya bean oil, tung oil, and menhaden oil, respectively. The tanks were weighed previous to and subsequent to the application of the oil, in order to determine the amount of oil applied. The tanks were individually connected up to a train of three Woulff bottles, the first of which contained 66° sulfuric acid, the second and third containing a saturated solution of barium hydrate. Vacuum was applied

common to each tank. The discolored sulfuric acid from each test had an acid odor. The bottles containing barium carbonate had an odor suggestive of aldehydes.

**RESULTS:** These tests indicate that the phenomenon of oxygen absorption which takes place when oils are spread in thin layers and exposed to the air, is accompanied by the evolution of considerable amounts of organic substances. Large quantities of carbon dioxide are simultaneously evolved.

**EXPERIMENT II.**—A series of paints was prepared from those opaque white pigments which are most widely used in the manufacture of exterior and interior paints (basic carbonate-white lead, basic sulfate-white lead, zinc oxide, and lithopone). The oil used was raw linseed oil. No turpentine or drier was added. The lead pigments were ground to a thick paste with 10 per cent of oil. The zinc pigments were ground to a paste with 15 per cent of oil. Oil in the proportion of about 7 gals. to the cwt. of paste was then added to each paint, the quantity of oil added in each instance being sufficient to make paints containing approximately 60 per cent pigment and 40 per cent oil. Each of the four iron cylinders described in Experiment I was then cleaned and painted on the inside with one of the four paints. An effort was made to spread the same amount of paint in each tank. After painting, the tops were placed upon the tanks and they were connected up to Woulff bottles containing various reagents as shown in Fig. 1. Uniform vacuum was applied to the end of each apparatus, and a 48-hour run was made. The air passing into the apparatus was scrubbed through a 10 per cent solution of caustic soda and then passed over soda lime in order to remove the carbonic acid present. The glass tubes coming from the ends of the cans were bent as shown in the illustration, to hold back any particles of paint which might be carried over, although such occurrence seemed highly improbable and such precautions unnecessary. A part of each exit tube was heated with the flame of a Bunsen burner, in order to



FIG. 1. APPARATUS FOR DETERMINING CHARACTER OF VAPORS FROM PAINTED SURFACES

1. Solution KOH, 10 per cent
2. Soda Lime
- 3.—Metal Cylinder Painted on Inside
4. Heated Glass Tube
5. Sulfuric Acid 66°
6. 7.—Barium Hydrate Solution

to the end bottle. The air entering the tank was scrubbed through a 10 per cent solution of caustic soda, and then passed over soda lime to eliminate carbon dioxide.

Soon after the tests were started, the sulfuric acid in the first bottle of each train became discolored. Within an hour the acid had assumed an amber color. The barium hydrate contained in the other bottles became opaque within a short time. At the end of a 2-day run, the sulfuric acid was dark red, and the barium hydrate solutions contained a dense white precipitate which proved to be barium carbonate. Each series of apparatus was disconnected and the coatings on the interior of the tanks examined. The amount of air passing through the tanks in 2 days was evidently insufficient to complete the oxidation of the oils which under normal conditions would have been quite dry in that time. The linseed oil was very soft and tacky. The soya bean oil was but slightly oxidized. The fish oil was somewhat tacky, but it had dried to a greater extent than the other two oils mentioned. The tung oil was very hard and dry. The smell emanating from the tanks was most unpleasant, being somewhat characteristic in each instance of the type of oil used. A certain nauseous smell, however, was

break up, if possible, any organic form of lead or zinc, which might be present in the vapors, since certain organic compounds of lead may not respond to tests for lead as made with ordinary reagents.

In every test the sulfuric acid contained in the bottle next to the tank was turned amber color within 5 minutes after the beginning of the test, thus showing that the drying paints were giving off considerable organic matter. After a 48-hour run, the acid in each bottle was dark red. The amount of carbon dioxide evolved in each test was considerable. No quantitative determination of carbon dioxide was made in any case. At the end of the experiment, the cans were re-weighed to determine the amount of oxygen absorbed. To the writer's surprise, there was recorded a loss of weight in one test, and but slight, if any, gains in the other tests. The basic carbonate-white lead paint lost 2 per cent by weight. The basic sulfate-white lead paint and the zinc oxide paint neither gained nor lost, the weight of the films remaining constant. The lithopone paint showed less than 1 per cent gain.

The bottles containing the sulfuric acid were removed from each train and the contents examined. Upon dilution with water,

the acid in the bottle, through which the fumes from the drying basic carbonate-white lead paint had been passed, became opaque. It was at first thought that this cloudiness of the diluted acid might be due to the presence of lead sulfate, formed by the absorption of volatile lead compounds eliminated by the drying paint. Alcohol was added to a portion of the liquid. It immediately became clear, thus indicating the absence of lead. A very thorough examination of the liquid was then made, and not a trace of lead was found. The sulfuric acid through which the vapors from the other paints were passed, was also examined. No metallic compounds were found. The experiments were repeated, the only refinement being that of introducing in front of the sulfuric acid bottles in the trains connected to the lead-painted cylinders, a bottle containing strips of filter paper saturated with sodium sulfide solution. The papers were not darkened in either case, thus giving further indication of the absence of lead compounds. In another experiment, one of the cylinders was painted with basic carbonate-white lead paint and the gases evolved were passed through a heated tube, finally being drawn through a 2 per cent solution of nitric acid. The test was run for forty-eight hours. The acid was evaporated on a steam bath. The residue was taken up with dilute acetic acid and a few drops of water. It

lead paints each required about 100 cc. permanganate solution. The acids in the trains connected to the cylinders painted with zinc paints required from 19 to 39 cc. of permanganate, that connected to the lithopone cylinder requiring the least amount. The solutions of acid thus oxidized were transferred to separatory flasks and shaken with ether. The ether solutions were thoroughly washed with water and then evaporated. In each instance a dark substance which had the appearance of heavy oil was left as a residue. This substance was found to be soluble in alcohol, in which solvent very acid reactions were given. No attempt was made to identify the acids present. Their complex nature would make such determination rather difficult, especially when working on small quantities.

RESULTS: 1. The above experiments indicate that the vapors from drying paints contain acids of a water-soluble nature. These acids apparently contain formic acid. The amount of such acid evolved may be influenced by the type of pigment present in the paint. The basic pigments are apparently more active than the neutral or inert pigments.

2. Organic acids of a fatty or aromatic nature are apparently evolved from drying paints. The amount evolved may bear some direct relation to the pigment present in the paints. The basic pigments apparently are most active in this respect.

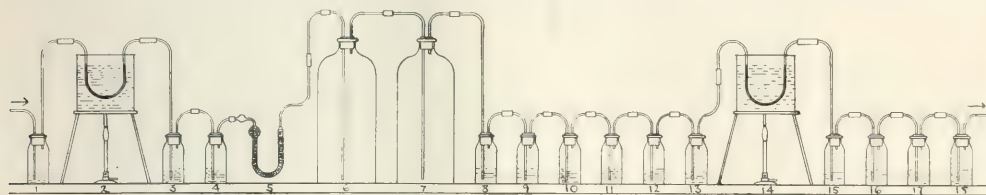


FIG. II—APPARATUS FOR DETERMINATION OF  $\text{CO}_2$  AND  $\text{CO}$  IN VAPORS FROM PAINTED SURFACES

1—Solution KOH, 10 per cent  
2, 14—Iodic acid in tube; Soya Oil Bath  
3, 4, 15, 16—1 per cent KI Solution  
5—Soda Lime

6, 7—Bottles Painted on Inside  
8—Fuming Sulfuric Acid  
9—Distilled Water  
10-13, 17, 18—Barium Hydrate Solution

was tested microscopically<sup>1</sup> for lead after the addition of copper acetate and potassium nitrate. No response for lead was shown in the test.

RESULTS: The results of these tests indicate that drying paints, containing zinc or lead pigments, do not emit volatile compounds of a metallic character.

When spread as thin films, oil-pigment paints are capable of evolving considerable amounts of organic substances without showing any material increase in their respective weights.

EXPERIMENT III.—Experiment II was repeated after cleaning the interior of the tanks and applying fresh coats of paint. The first Wouffli bottle in each train contained distilled water. The second bottle contained 66° sulfuric acid. After a 48-hour run, the contents of the first bottle in each train were examined. The water in each instance was acid in reaction. There were required for neutralization from 1 cc. to 14 cc. of  $N/10$  KOH. The water in the bottle connected to the cylinder painted with lithopone showed the lowest amount of acid, while the water connected to the cylinder painted with basic carbonate-white lead showed the largest percentage of acid. The presence of carbon dioxide in the water may partially account for the acidity of these tests. A portion of the neutralized acid was tested qualitatively for the presence of aldehydes. Small amounts of aldehydes were found present. Formates were also found present. The sulfuric acid in each of the four bottles was diluted with water and titrated with  $N/10$  potassium permanganate to determine the amount of reducing substances present. The acids in the trains connected to the cylinders painted with white

The aldehydic reducing substances and the acids which are evolved from paints are, no doubt, responsible for the odors which are coincident to the drying of paints. In the writer's opinion, however, there are also evolved substances of a more poisonous nature. Inasmuch as large percentages of carbon dioxide are formed, it is at least possible that carbon monoxide may also be produced. The following experiments were designed to determine whether this gas is really formed

EXPERIMENT IV.—After many attempts to devise a suitable apparatus in which to determine the percentage of carbon dioxide or carbon monoxide which might be evolved by drying paints, the apparatus shown in Fig. II was found to be most satisfactory for the purpose. The first experiment made with this apparatus was conducted upon raw *linseed oil*. The interiors of two carefully weighed glass bottles, each having a capacity of one gallon, were coated with linseed oil. The oil was poured into each bottle and allowed to flow over the entire area of the interior, this being accomplished by revolving the bottle. After draining out the superfluous oil, the bottles were re-weighed to determine the amount of oil used for the test. Cork stoppers carrying glass air-tubes, were then inserted. The stoppers were thickly coated with paraffin to make them air-tight. The apparatus was connected up as shown in Fig. II. Vacuum was applied at one end. As the purpose of the experiment was to determine the presence and amount of carbon dioxide or carbon monoxide in the vapors from the oil, the air entering the bottles was first freed of its content of carbon dioxide and carbon monoxide. This was accomplished by first

<sup>1</sup> Page 167, "Lead Poisoning and Lead Absorption," Legge and Goadby. Longmans, Green & Co., Publishers.



scrubbing it through a solution of caustic soda in order to remove the carbon dioxide. The air was then run through a U-tube containing iodine pentoxide heated in a bath of soya oil to 150° C. at which temperature carbon monoxide is oxidized to carbon dioxide.<sup>1</sup> The iodine liberated was absorbed in a 1 per cent solution of potassium iodide and the carbon dioxide formed was taken up by the caustic soda and soda lime in the subsequent train of apparatus.

After the tests had been running for 15 minutes, the fuming sulfuric acid in bottle 8 was turned amber color, showing that organic substances evolved by the oil were being absorbed. The absorption of these organic vapors by the sulfuric acid prevented such vapors from interfering with the subsequent train of liquids in which the percentage of carbon dioxide and carbon monoxide were to be determined. Bottle 10 containing saturated barium hydrate, the strength of which was determined by titration, showed a slight precipitate of barium carbonate at the end of the first 10-minute run. At the end of a 5-hour run, bottles 10-11 and 12 showed quite a noticeable deposit of barium carbonate. Bottle 15, containing potassium iodide, did not change color until the tests had been under way for over an hour. At that period the reagent became slightly yellow, showing that some iodine had been carried over into this bottle, thus indicating the presence of carbon monoxide in the vapor. The barium hydrate in bottle 17 at the same time became cloudy, showing that traces of carbon monoxide which had been evolved, had been oxidized and absorbed as carbon dioxide. The percentage of carbon monoxide evolved by the drying oil in five hours was determined by titrating the barium hydrate contained in bottles 10 to 13 with *N*/10 oxalic acid, using phenolphthalein as an indicator. The titration was made direct. The amount of carbon dioxide found present was 0.016 per cent. The amount of carbon monoxide was not measurable, although it was shown to be present in traces.

**RESULTS:** This experiment indicates that linseed oil in drying gives off traces of carbon monoxide.

**EXPERIMENT V.**—Experiment IV was repeated, coating the interior of the bottles in this case with basic carbonate-white lead paint in place of raw linseed oil. The test was run for five hours. The amount of carbon dioxide produced in that time was 0.0305 per cent. The carbon monoxide evolved amounted to 0.006 per cent. The experiment was made with basic sulfate-white lead paint in place of basic carbonate-white lead. The experiment was accidentally interrupted.

The experiment was again repeated, using zinc oxide paint in place of the white lead paint. The amount of carbon dioxide evolved was 0.0292 per cent. The amount of carbon monoxide evolved was 0.0039 per cent.

The experiment was again repeated, using lithopone paint in place of the zinc oxide paint. The amount of carbon dioxide evolved was 0.022 per cent. A mere trace of carbon monoxide was found.

Experiment V was repeated with a basic carbonate-white lead paint. The first bottle leading from the painted bottles contained fuming sulfuric acid to intercept and collect the organic vapors. The second bottle contained water. The third bottle contained alkaline bisulfite solution to collect any traces of aldehydes which, if evolved by the paint, might possibly escape absorption by the sulfuric acid. The fourth and fifth bottles contained water and caustic soda solutions, respectively, the latter to collect the carbon dioxide or phenols evolved. The vapors passing from the last bottle were passed through a U-tube containing small lumps of caustic potash. The U-tube was immersed in hot soya oil. At the end of a 5-hour test, the U-tube was removed from the hot oil and the lumps of caustic potash removed and examined for the presence of formates which,

if present, would indicate that absorption of carbon monoxide had occurred. After dissolving the potassium hydrate in water, making acid with tartaric acid and distilling over barium carbonate suspended in water, the filtrate from the barium carbonate was treated with a small percentage of bichloride of mercury. After the solution had stood over night, a very faint precipitate of calomel was observed, indicating the presence of carbon monoxide.

**RESULTS:** These experiments would tend to show that the highly basic pigments stimulate the evolution of organic substances from linseed oil paints, especially influencing the amount of carbon dioxide and carbon monoxide evolved.

The amount of air entering the painted bottle in a 5-hour run was insufficient to cause any marked oxidation. This explains why such small amounts of carbon dioxide and carbon monoxide were obtained. The extremely small quantities present made the analytical determinations a matter of great care. Tests extending over a greater period should be made, in order to substantiate the figures presented. The writer is designing another type of apparatus in which it is hoped more accurate determinations may be made.

**EXPERIMENT VI.**—In this experiment a portion of lithopone paint was reduced with 15 per cent of turpentine and then applied to the interior of the bottles. At the end of three hours, the percentage of carbon dioxide evolved was 0.04, while the percentage of carbon monoxide was 0.003. This result may be due to the oxidation of the turpentine.

**RESULTS:** Turpentine apparently accelerates the reactions which are responsible for the formation of volatile products from drying oils. The oxidative properties of the turpentine are probably responsible for this result.

#### GENERAL DISCUSSION OF RESULTS

The results obtained in Experiment II, in which the paint films showed but slight if any increase of weight at the end of the tests, are interesting. They may be partially accounted for by assuming that the amount of air passed through the tanks in 48 hours was very small. It will be well at this point to discuss the experiments on linseed oil and oil-pigment paints, as made by Sabin.<sup>1</sup> He describes a series of tests in which various paints were applied to small glass plates, the increase in weight shown by the paints being recorded at different periods. At the end of 7 days, raw linseed oil showed a gain in weight of 18 per cent, while white lead paint showed a gain of approximately 15 per cent.

The writer carried out a similar series of tests with a set of paints made up with 60 per cent of pigment and 40 per cent of raw linseed oil. The gain in weight of the films at the end of 7 days was as follows:

	Per cent
Linseed oil.....	14.0
Corroded white lead.....	6.4
Sublimed white lead.....	7.1
Zinc oxide.....	5.4
Lithopone.....	5.9

These tests indicate that oil-pigment paints do not gain in weight to the same extent as raw linseed oil. Heretofore, however, investigators have not given consideration to the possibility that pigments may stimulate not only those processes which cause the oil to increase in weight through the absorption of oxygen,

<sup>1</sup> Method Used for Examination of Tunnel Gas," by Dr. A. Sechell, Hygienic Laboratory, Washington, D. C.

<sup>1</sup> THIS JOURNAL, 3, 84.

but also those processes and reactions which cause the oil to eliminate volatile substances, which might detract materially from the weight of the paint. In this connection it is of interest to cite the tests of Olsen and Ratner<sup>1</sup> upon the drying of linseed oil. They record a gain in weight of 18 per cent at the end of approximately 10 weeks. They also showed the elimination of approximately 5 per cent of carbon dioxide and 15 per cent of water.

#### SUMMARY OF CONCLUSIONS

I. When linseed oil or similar drying oils are spread in thin layers, the absorption of oxygen which takes place is accompanied by the evolution of considerable amounts of carbon dioxide and organic substances. Carbon monoxide is also evolved in small amount.

II. Oil paints containing lead or zinc pigments do not emit volatile compounds of a metallic nature.

III. Drying paints evolve water-soluble acid substances such as formic acid, as well as acid substances which are apparently of a fatty nature. Carbon dioxide and carbon monoxide are also present in the vapors from the drying paint. The type of pigment used in the paint may directly affect the amount and character of the volatile substances produced. Basic pigments apparently stimulate the evolution of such products.

IV. Aldehydic substances are present in the vapors from drying oil paints. These substances probably have a marked bactericidal effect upon pathogenic bacteria and would thus account for the sanitary value ascribed to oil-pigment paints.

The writer desires to thank H. C. Fuller, L. G. Carmick and the staff of The Institute of Industrial Research for their assistance in carrying out the above experiments.

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WASHINGTON

#### METALLOGRAPHY AS APPLIED TO INSPECTION

By WIRT TASSIN

Received December 11, 1913

The sudden failure of engineering structures of metal, the static physical tests of which, before use, pointed to the good quality of the materials, is well known. Such failures have usually been attributed to a so-called deterioration known as "fatigue."

Whether or not repeated stresses below the elastic limit of the metal can set up such a deterioration may be questioned. One fact has however been proven beyond all question, and that is that in any metal there are always present certain structural conditions, the influence of which are either favorable or unfavorable to "fatigue."

The character of these structural conditions is indicated in part only, and then often by chance, by the static and dynamic tests. It may, however, be completely revealed by metallographic methods, that is, by the study of the structure of the metal as seen on the etched surface under the microscope.

The possibilities of metallographic methods as an additional safeguard to determine quality have been

recognized, but their usefulness has been limited by the lack of protability in the appliances necessary for their use. This has made it difficult, if not impossible, to study the forging, the casting or the bar as a whole, with the result that the metallographic field has been limited to the examination of more or less small specimens cut from the piece and which, like the bar used for the machine tests, may or may not be representative of the whole.

It is the purpose of this paper to describe a complete metallographic outfit which is portable and may be used either in the mill or the laboratory and is serviceable for the study of the forging, the bar or the casting as a whole; to give certain types of structure found in the ferrous metals; to give a list of certain probable causes for failure and to outline a scheme for their detection and thus supplement other methods of testing.

#### THE APPARATUS

The apparatus<sup>1</sup> consists of a microscope, illuminating device and a camera, all self-contained, Fig. 1, *A*, *B* and *C*.

The microscope, Fig. 2, consists of a barrel, *b*, and a draw-tube, *d*, mounted on a handle arm provided with a coarse and a fine adjustment. Attached to the barrel is a shoulder, *c*, which holds a rod, *r*, controlled by a set screw. The base of this rod rests on the pinion head of the handle-arm and when locked with the set-screw prevents the coarse adjustment from overrunning when using the camera. The whole is carried on a base which is the stage. Through the center of the stage is a 1-inch circular opening which affords free space for the objective when examining large masses below it. Leveling screws are provided, one in each of the four corners of the stage, which permit the adjustment of the microscope perpendicular to nearly any surface.

The illuminating device consists of an arm, *a*, in Fig. 2, which locks into the microscope barrel by means of a threaded collar. The arm serves to carry the condensing arrangement made up of a telescope tube, *h*, which carries the lenses. The tube is mounted in a sleeve, *y*, provided with a set-screw to lock it in any position. A hanger, *k*, from the arm is attached to this sleeve by means of a trunnion controlled by a set-screw which permits the tube as a whole to be tilted at any angle. A vertical adjustment is provided for by a set-screw at the outer extremity of the arm. The rear of the telescope tube carries a shield, *xx*, provided with clips to hold the source of light when electricity is used and is slotted to hold a rod and a movable lamp carrier when gas is used.

The source of light may be an acetylene jet or an electric lamp.

When acetylene is used the gas may be obtained from a generator or from a prestolite tank. The support for the lamp is a rod which locks into the slot in the shield of the illuminator. On the rod is placed the movable carrier for the source of light, see *B*, Fig. 1.

When electricity is used the lamp is carried in a socket fixed in an insulated metal hood and held in

<sup>1</sup> *J. S. C. I.*, **31**, 937 (1912).

<sup>1</sup> Manufactured by Bausch and Lomb, Rochester, N. Y.



FIG. 1—A



FIG. 1—B

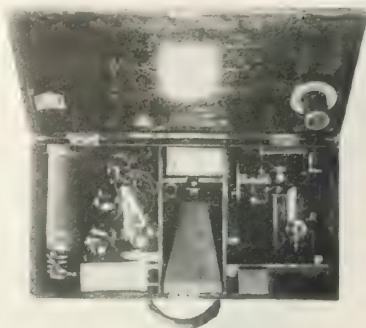


FIG. 1—C

position with reference to the lenses of the condensing train by clips fastened to the shield of the illuminator; see A, Fig. 1.

The current may be obtained from an accumulator or by cutting down the lighting current. A lamp bank to reduce a 110 volt current is wired as in Fig. 3. The lamp resistance needed for the various candle power 6 volt tungsten miniature lamps is:

Two 32 and one 16 c. p. carbon lamps for a 6 volt, 16 c. p. tungsten miniature.

One 32 and one 8 c. p. carbon for a 6 volt, 8 c. p. lamp.

One 32, or two 16, and one 4 c. p. carbon lamps for a 6 volt, 6 c. p. tungsten miniature.

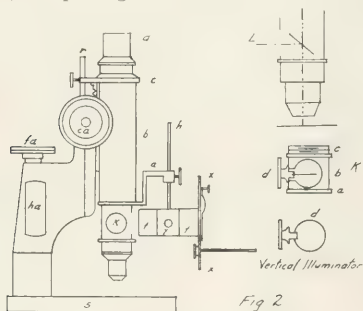


Fig 2

One 16 and one 4 c. p. carbon for a 6 volt, 4 c. p. tungsten.

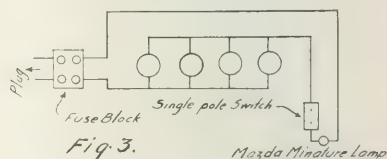
Any of these candle power tungsten lamps may be used but the one recommended is the 6 volt, 16 c. p. lamp known as "Headlight Mazda, No. 68, 12 G., candelabra base."

To get the light from the condensing train through the objective use is made of a device known as a "vertical illuminator," K in Fig 2. This device screws into the barrel of the microscope below the hanger which carries the condensing train. Turning the plate d of the illuminator to some desired angle reflects the illuminating ray, which enters the aperture, down upon the surface of the metal. This in turn reflects the light up through the barrel to the eye.

A "quick-acting nose piece" is fitted to the lower end of the vertical illuminator. This device permits

of a ready change of objectives without an unscrewing motion and consists of a clamp operated by a spring controlled by two handles. Pressing the handles opens the clamp and permits the insertion of a ring, one of which is provided for each objective and to which it has been previously fastened.

The camera, see Fig. 1, is connected with the barrel of the microscope by a tube which slips in and out like the draw tube of the microscope and may be removed with the same ease. The camera moves with, and becomes part of the barrel and any degree of focusing is possible. The distance between the eye piece and the ground glass is a constant so that the amplification is standard for each magnification. To use the camera the draw tube of the microscope is removed and the tube of the camera inserted.



The apparatus lends itself readily to all forms of metallographic work and is adapted to the needs of the inspector, the engineer of tests and the metallurgist. It may be used in the mill or the laboratory and is equally adapted for the study of the mass, Figs. 4, 5 and 6, or the small specimen. It is used both for visual examinations and for making photographic records. It is portable, self-contained and compact.

#### METALLOGRAPHIC METHODS

**SAMPLING.**—By sampling is meant the location and number of areas to be polished. It is not necessary nor practicable to polish the entire surface of the mass provided that a sufficient number of small areas be taken which shall properly represent it. In selecting these areas it is desirable to follow some fixed rule and always prepare the surface at definite positions which shall be the same for the same kind of objects so as to be of value for comparison. This is especially desirable when grain size is to be taken into consideration as the grain may vary greatly in different parts of the work as from the thick to the thin parts of a casting.



In billets the cross section at each end should be taken, together with several areas parallel to the direction of the work and preferably on two or more sides. With rounds prepare a cross section at each end and several others parallel to the direction of the work. With flats take along the center lines of the several sides. With hollow forgings and similar material areas along the outer and inner surfaces in the direction of the work should be chosen together with two or more cross sections at each end. With castings both thick and thin parts should be selected and where the cope and drag can be distinguished, sections along each should be taken together with areas in those parts which have to take the major part of any sudden load, as trunnions.

Sections should never be prepared too near any distorted part as a sheared edge or punched hole. With annealed material, especially with castings where the soaking has been prolonged, care should be taken to get below that part decarbonized by the action of the flame.

**CLEANING.**—After polishing and before etching clean the surface with cotton moistened with alcohol or gasoline.

**ETCHING.**—After cleaning, the surface is now ready to have its structure developed. This is usually done by means of some reagent which attacks or colors some constituent of the metal more than it does others. For the ferrous metals a 10 per cent solution of picric acid in 95 per cent alcohol will be found the more useful. Soak some absorbent cotton in the solution. Take up the cotton with a pair of tongs or tweezers and allow the excess acid to drain off. Place the cotton on the surface to be etched and move it back and forth till the desired depth of etch is obtained. The degree of temperature affects the speed of etching, the colder it is the longer the time; with 55 to 70 degrees of temperature about 20 seconds is sufficient.

After etching wipe off the acid with cotton or clean, soft waste, then clean thoroughly with cotton moistened with alcohol.

Care must be taken that the etching fluid covers the



FIG. 4



FIG. 5



FIG. 6

The size of the sections polished should be about three inches wide by about twelve inches long.

**POLISHING.**—This is done by wheels and buffs driven by an electric or a pneumatic grinder, one or the other of which is usually to be found in any mill. When preparing a surface the following treatment has been found satisfactory for most purposes: If the surface is very rough grind down with a 24 grain emery wheel, follow with a cloth wheel charged with 60 emery, then use a similar wheel charged with 120 emery, follow with a buff charged with washed flour emery paste and finish with a buff charged with rouge.

The above procedure requires about 15 minutes to finish an area 3 inches by 12 inches and will give a surface that is perfectly satisfactory if the etching is done with picric acid or iodine. It is not necessary that the surface should be free from scratches but it is necessary that the scratches should all lie in the same direction.

whole area and that the saturated cotton is moved back and forth with a rapidity sufficient to insure the even distribution of the acid over the surface at all times as otherwise there may be variations in the character of the etch which may give rise to false conclusions. This variation in the etch is less likely to happen with picric acid than with other etching mediums.

**THE VISUAL EXAMINATION.**—With the unaided eye look for streaks or areas which are differently colored. Carbon-rich areas will usually appear darker and carbon-lean areas lighter than the rest of the surface. In general the segregations of the alloy elements will also be indicated by a color difference. Heat and forging cracks are commonly rendered visible as well as pipes, seams, shakes, flow lines, cold shuts, welds, etc.

When making the microscopic examination the instrument should be leveled, if necessary, by means of the screws on the stage.

The field should be clear, distinct and free from any haze, glare or image of the lamp. Should any of these appear the illumination is faulty and must be corrected. To adjust the illumination the condensing train as a whole should be raised or lowered so that the plane of its lenses is centrally in line with the opening of the vertical illuminator. Then shift the angle of the mirror in the illuminator, or the source of light.

It is recommended that but three sizes of objectives and one size eye piece be used, a 32 mm., a 16 mm., and an 8 mm. Bausch & Lomb objective and a 7.5x eye piece. These will give magnifications of 30, 65 and 150, respectively. Where higher magnifications are desired eye piece magnifications are preferable to the use of higher powered objectives and a magnification of 315 can be obtained with a 15x eye piece and the 8 mm. objective.

Care should be taken that the entire area etched should be gone over and that part selected for the photograph should be strictly representative.

**PHOTOGRAPHING.**—When inserting the camera it is advisable to rack the tube of the microscope well up away from the surface of the metal before removing the draw tube and attaching the camera. This will prevent the chance of damaging the objective by jamming it against the metal. After attaching the camera it is brought in focus by the coarse adjustment. The rod *r*, in Fig. 2, is brought squarely down on the pinion head and locked with the set-screw; this prevents a change of focus when changing plate holders. Further should the tube rack too easily, tighten it by setting down the screws holding the pinion of the coarse adjustment. The final focus is fixed with the fine adjustment, the sharpness of the image as seen on the clear spot of the ground glass being determined with a pocket magnifier.

All photographs should be taken with the eye piece in the camera and it will be found convenient to have two 7.5x eye pieces, one for the draw tube of the microscope and one to be kept in the tube of the camera.

The plates used should be fast and give good color values and to this end Seed's "L Ortho" are recommended. The size of the plate is  $3\frac{1}{2} \times 3\frac{1}{2}$  inches and the image is about  $3\frac{1}{4}$  inches.

The time of the exposure depends upon the character of the surface and the plates used. For steel, using the above plates it will not average over 10 seconds.

After exposing it is always well to verify the focus by looking through the ground glass and thus make sure that it has not been overrun as a result of changing the plate holder.

**DEVELOPING.**—The plates may be developed in the ordinary way with any of the developers on the market. It is suggested that "Ingento edinol hydrochinon developing tablets" be used because of their adaptability for dish and tank developing and for printing.

Where a dark room is not available an Ingento changing bag will be found an efficient substitute while loading and changing plates. Such a bag together with two tanks makes it possible to develop and fix the plates without leaving the work.

For tank developing in addition to the Ingento developer referred to the following formulas may be used for 20 minute developing at 60 to 70 degrees:

Hydrochinon.....	90 grains
Sod. sulfite (anhydrous).....	400 grains
Sod. carbonate anhydrous.....	300 grains
Water.....	30 ounces

To each part of this stock solution add three parts of water before using.

Edinol.....	145 grains
Sod. sulfite (anhydrous).....	300 grains
Sod. carbonate (anhydrous).....	300 grains
Water.....	40 ounces

To each part of this stock solution add three parts of water before using.

The plain fixing bath of 4 ounces of "hypo" to 16 ounces of water may be used with any of these formulas; the following is, however, to be preferred:

Water.....	96 ounces	Chrome alum.....	32 ounces
Sol. 1 { Hypo.....	2 pounds	Sol. 2 { Sulfuric acid.....	1 ounce
Sod. sulfite.....	2 ounces		

Dissolve 1 and 2 separately, then slowly pour 2 into 1 with constant stirring.

It should be remembered that for the permanency of the negative, a complete fixing followed by a thorough washing and a slow drying is an essential. Occasionally prints are desired as soon as possible. Then the plate after fixing may be quickly rinsed with water, soaked in alcohol and dried in 15 minutes. After the prints are made the plate should be washed thoroughly in water to remove any traces of the fixing bath which may remain and again dried.

**CARE OF NEGATIVES.**—The negatives should be kept in envelopes plainly marked with sufficient data to identify them at any time.

Most micrographic negatives contain areas that are not needed or are out of focus. It will be found convenient to use a mask to cut out such parts when printing from them. Time will be saved if each negative is matted out permanently. To this end it will be found convenient to prepare a template out of  $\frac{1}{16}$ " sheet steel or brass which shall be a 3 inch square with a  $2\frac{7}{16}$  inch circular central opening. Laying the template and a suitable piece of paper on a sheet of glass any number of masks may be quickly and easily cut with a sharp knife. One of these masks is then pasted on the film side of the negative thus always ensuring the same field.

**PRINTING.**—Any of the gaslight papers may be used. The glossy papers give better detail but they are liable to be scratched during manipulation, and require squeegeeing to get the best results and are to this degree not so desirable as the velvet or satin finishes.

In printing, where electric light is available, a printing or developing lantern as shown in Fig. 7 will be found convenient. Throwing the switch one way gives the exposure, the other way gives the developing light. With two 100 c. p. Mazda lamps the time of exposure will rarely exceed 12 seconds.

The prints after developing should be thoroughly fixed and washed and preferably dried between blot-

ters. If they are needed quickly they may be soaked in alcohol and dried within 15 minutes.

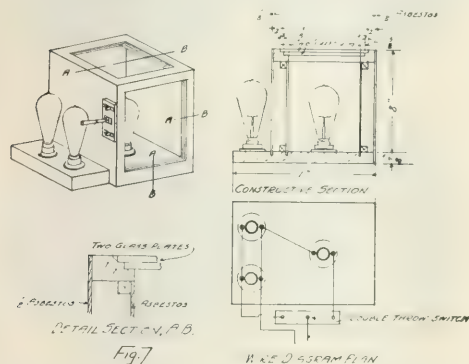
**RECORDS.**—It is always well to make notes at the time of the examination as the eye is better than the best of photographs.

The records should include remarks as to appearance, opinion as to what the area indicates and other details. Note the number and description of the piece, location of the area examined, the etching medium and the time of etching, the number of the objective and eye piece and the magnification.

#### TYPES OF STRUCTURE

The structure of steel may be profoundly modified by the rate of cooling from a high temperature, the degree of re-heating and the amount and kind of work to which it has been subjected. The several structures so obtained may each be referred to a type.

In a steel obtained by the simple solidification of the liquid metal followed by a slow and undisturbed



cooling the grain size will be large; Fig. 8. If now the metal be re-heated to some temperature below its melting point and cooled slowly without mechanical work being applied, there will be a corresponding change in the grain; Fig. 9.

In any steel, other things being equal, the smaller and more uniform the grain the better the physical properties and the size and uniformity of the grain is influenced by heat and by work.

Steel is heated to give the plasticity required for rolling or forging. It is heated to relieve internal stress but an improper heating or an interrupted cooling may set up such stresses and even cause rupture. It is heated to give hardness or to take it away. The higher the temperature from which it cools the larger will be the grain. Heating to some certain temperature will give the finest grain possible and all previously existing structures, however coarse, will be obliterated. Heating for a longer period or a shorter time at too high a temperature, or a long heating at too low a temperature will coarsen the structure. Too rapid heating or too rapid cooling or an unequal rate of cooling may set up internal stresses and cause rupture.

With steel castings the effect of these conditions is shown by Fig. 10, the structure of the metal as

cast; Fig. 11, the structure as properly annealed; Fig. 12, the effect of annealing at too low a temperature.

With rolled or forged material they are shown by Figs. 13, 14 and 15 which show the normal grain as properly annealed and the effect of higher temperatures upon it.

The size of the grain and its uniformity is also affected by the amount and kind of work to which the metal has been subjected. Work may be applied in two ways, hot or cold. Hot working when finished at some certain temperature gives a small grain and the most tough and ductile metal. If the finishing temperature be too low the grain will be more or less distorted and if the work be carried far enough the metal will have a tendency to become brittle or to split along the direction of the work. The higher the finishing temperature the coarser the grain and the weaker and more brittle the metal. Cold working distorts the grain and renders it fibrous.

The effect of work can be seen best on the cross section. Thus in a hammer-forged piece if the work be applied during the proper temperature and is vigorous enough, each blow will penetrate the center and the grain will be practically uniform throughout. If the work is not vigorous enough, or the metal hotter in one portion than in another there will be more or less marked differences in grain and there may be alternate layers of hard and soft metal if the heating be followed by work with portions of the interior colder than the exterior or if the work be applied locally when the exterior is much colder than the interior. Fig. 16 shows the fracture of a hammered piece having the interior much hotter than the exterior.

The tendency of the several constituents of steel to segregate is known and in general they are to be regarded as elements of weakness. Figs. 17 and 18 show the appearance of such segregations to the unaided eye after etching; Figs. 19 and 20 their appearance under the microscope. These areas are in general relatively large and they can be seen best with the lowest powers; in fact the higher powers, because of the smallness of the field, often fail to show the structural differences between the segregated and non-segregated areas.

Slag is liable to be found in any steel and when sparingly distributed in isolated particles may be disregarded, but when occurring in any amount it is always a source of weakness. Fig. 21 is an illustration of its occurrence under conditions where it is an element of danger.

Sulfides, Figs. 22 to 24, like slag, may be found in any steel and when sparingly distributed in isolated or minute particles may be disregarded, but as the amount increases the element of weakness increases.

**STRUCTURE OF SOUND STEEL.**—Steel of normal composition and treatment will show after etching a surface free from segregations and laminations. The structure will be regular and uniform and the grain will show a gradual increase in size from the outside to the center as the result of work. The boundaries of the grain will be quite regular in outline with little or no signs of ingotism, or incomplete grain refining. Slag



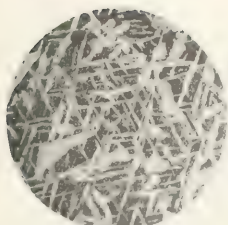
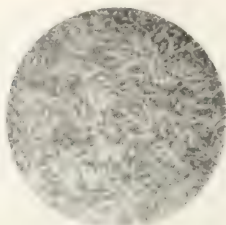
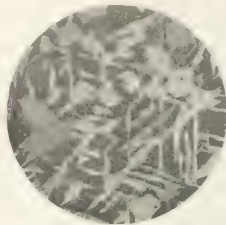
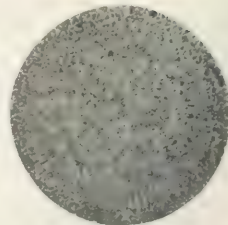
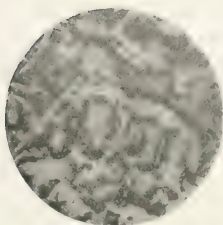
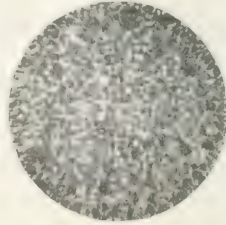
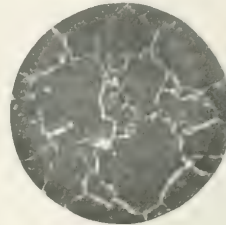
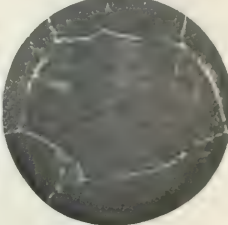
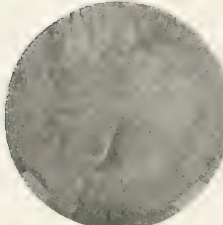
FIG. 8  $\times 65$ FIG. 9  $\times 65$ FIG. 10  $\times 65$ FIG. 11  $\times 65$ FIG. 12  $\times 150$ FIG. 13  $\times 65$ FIG. 14  $\times 150$ FIG. 15  $\times 150$ 

FIG. 16

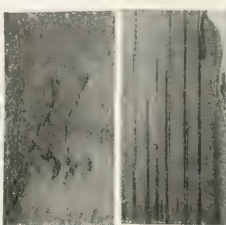


FIG. 17

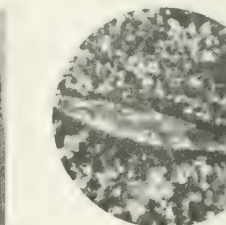
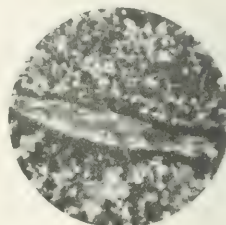
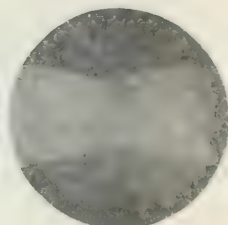
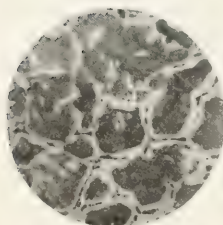
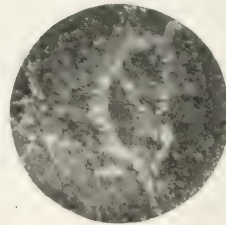
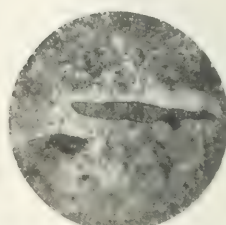
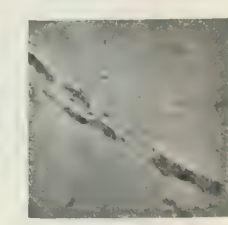


FIG. 18

FIG. 19  $\times 30$ FIG. 20  $\times 30$ FIG. 21  $\times 150$ FIG. 22  $\times 150$ FIG. 23  $\times 150$ FIG. 24  $\times 30$ 

and sulfides are absent or only sparingly present and in isolated particles.

When cold rolled or drawn the grain will be distorted in those parts affected by the work but there will be no cracks or fissures either in or between the grain nor any "loosening."

**STRUCTURE OF UNSOUND STEEL.**—The causes which may give rise to unsoundness and failure are sand splits, seams, pipes, blowholes, cavities and honey-comb, all of which during work are extended as cracks. Etching develops these defects and usually renders them plainly visible to the unaided eye.

Ingotism, incomplete grain refining and failure to

destroy an existing coarse structure—these conditions if present to any extent imply internal stress, lack of cohesion, liability to cleavage and brittleness.

Lack of uniformity of the grain in which those nearer the center are smaller than those further away from it—such a structure is common to material which has been heated either too high or too long. Too high heating coarsens the grain; Figs. 13, 14 and 15. In general any marked lack of uniformity of the grain implies a lowered resistance to a repeated or a suddenly applied load.

Segregations of certain essential components of the steel as the carbon or the alloying elements—Figs. 17 and 18 give rise to areas each of which have

different physical properties. The presence of such areas implies a lack of continuity in the metal, since the junction lines between them are more or less sharp; Figs. 19 and 20. Such areas when under a load have a tendency to slip one upon the other, thus setting up a rupture. Their presence is revealed microscopically and macroscopically by etching. When studying them under the microscope the use of the lowest powers is advised.

Layers, streaks or patches of various impurities as slag, sulfide, etc.—all of these are less ductile and more brittle than the steel.

#### METHOD OF EXAMINATION

Sample, polish and etch. Examine macroscopically for pipes, cracks, seam, laps, blow-holes, honeycomb or sponginess, welds, segregations and laminations (especially on the cross section), flow lines, excessive slag and sulfide areas, cinder, etc., Examine microscopically for lack of uniformity of grain, coarseness, ingotism or incomplete refining. Look for slag and sulfide areas with reference to their abundance and distribution.

#### CONCLUSION

It can be shown that a large piece of work can be spot polished in eight or more different places with but little, if any, more expense and time than it takes to prepare a standard test bar; that there is a relation between structure and physical properties. It follows that given sufficient experience and a set of standards, metallographic methods will give information that cannot be obtained conveniently by any other method of inspection.

It should be stated that metallography is not intended to replace other methods of test and inspection but to supplement them and thus afford an additional safeguard against failure.

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### MAHONE PETROLEUM

#### Its Recent Origin, and the Origin of Petroleum in General

By CHARLES F. MABERY

Received December 22, 1913

Six years ago I was invited to visit a section of the Valley of the Mahoning River in Mahoning County, Ohio, where a deposit of petroleum had been known in Milton Township for several years, and where an open well was still to be seen from which oozed a small stream of thick oil. At the time of this visit, several wells had recently been drilled over an extended area, and were producing a considerable supply of oil. But on account of faulty operation and mismanagement, these wells soon afterward became inoperative and the entire field was closed until some years later. Several wells were then to be seen on a farm bordering on the river valley, the property of Mr. R. Wiesener, from which some years earlier oil had been pumped freely and sold as a lubricant without refining.

On learning of the shallow depths at which this petroleum was reached, my interest was naturally aroused with reference to its origin, and I made several subsequent visits to become better acquainted with its

occurrence, in connection with a laboratory study of the oil which seemed especially inviting, for it evidently differed very materially in its composition from the other well known varieties of petroleum. It had the further attraction that, associated with the petroleum in or near the river valley, there were extensive beds of high-grade bituminous coal, sections of which in the adjoining Township of Palmyra, were mined on an extensive scale. In a narrow section of the valley, approximately one hundred feet in width, where the river had cut its way down from a considerable height, exposing an abrupt vertical section of the geological formations, a vein was exposed, three or four feet in thickness, of partially weathered carboniferous deposits with the accompanying shales so friable that they were easily crushed in the hands. Analysis showed that these deposits contained nearly fifty per cent of pure carboniferous material. It, therefore, seemed probable that the coal and the oil were of a common origin, which, in connection with the shallow depths of the oil strata, less than 150 ft., presented an inviting opportunity to study the origin of petroleum at close range.

#### GEOLOGICAL OCCURRENCE OF MAHONE PETROLEUM

The Mahoning River rises in Columbiana County, and flowing sinuously through Portage, Trumbull, and Mahoning Counties, finally enters the Ohio River. In Mahoning County the valley is a few miles in length, and its greatest width is 2800 ft. The wells drilled for oil vary in depth from 135 to 150 ft.; in one well the oil sand was reached at a depth of 115 ft. According to the report of the driller, the surface layer extends in a depth of 20 ft. to a bed rock of shales that are continuous to the oil-bearing sand. These shales are partly light and partly dark in color, and just above the upper layer, below the surface silt is a bed of sand and below that a bed of shale impregnated with bituminous carbon. The oil sand composed of rather coarse granules of very pure quartz is overlaid by a soapstone shale 14 ft. thick, and it extends to a depth of 105 ft., of which the upper coarser layer, 16–18 ft. thick, carries the oil above a large volume of water. Below this sand is a brown shale sixty feet thick, and below this a lighter shale extending to the Berea Grit.

So far as it appears from the 25 or more wells that have been drilled by the Mahone Oil and Gas Company, there are no restricted pockets in the oil strata, but a somewhat regular anticlinal and synclinal formation, the anticlinals approximately 20 ft. in height and 200–300 ft. in diameter. On account of the inertness of the crude oil, special care is necessary in drilling, and particularly in pumping: it is raised with some water into large settling tanks and the water drawn off. The daily yield from a single well is small; the largest daily output from any one well has been 8 barrels. There is evidently nothing especially striking in the formations connected with the occurrence of this petroleum, except the shallow depths at which the oil is found, and the absence of any complicated conditions connected with its origin.

As mentioned above, the Berea Grit appearing in

this section as an underlying formation suggested the probability that the abundance of oil and gas elsewhere in this oil strata should likewise promise similar yields in this field. Accordingly a well was started with the intention of drilling to a sufficient depth to reach any possible deposits in this section of the Berea Grit. This well has been carried to a depth of 1800 ft. and will be continued with the expectation of reaching an abundant flow of gas and the lighter Berea Grit oil.

#### PHYSICAL CHARACTERISTICS AND COMPOSITION OF MAHONE PETROLEUM

Soon after the first wells were drilled, specimens of the oil placed in my hands for examination appeared to be so unlike any that had been brought to my attention, that I undertook a thorough study of the crude oil and the products to be obtained from it, both on account of its interest from a scientific point of view and the possibility of the preparation from it of commercial products. After three years with the aid of two assistants, although much has yet to be done on the composition of its constituents it seems advisable to place on record the accumulated observations on the nature of the crude oil.

This petroleum is quite dark, approaching black in color and it has scarcely any odor. In consistency it is very thick and viscous; its specific gravity taken from samples pumped at different times during three years gave, at 20° C., in four samples:

I	II	III	IV
9057	9036	9040	9036

showing practically no variation in different sections of the field during this period. Its extremely high viscosity—928—explains its former use as a lubricant without refining. Its refractive index as determined by the Abbé refractometer is 1.4878, a value unusually high as compared with other varieties of petroleum. So much attention has recently been given to the optical activity of petroleum, and rotation has been observed in so many varieties of crude oil and products of refining, that it became necessary to ascertain whether this petroleum was also optically active; but in neither the crude oil nor in any products separated from it could the slightest effect on the polarized ray be detected. Perhaps this is what should be expected in view of its composition which is much less complex than that of other varieties of petroleum, in fact consisting (as will be shown later) of a comparatively few hydrocarbons, so far as examined only of the series  $C_nH_{2n-2}$  and  $C_nH_{2n-4}$ .

In testing the crude oil for sulfur by decomposition with sodium and comparing the color given by potassium nitroferrocyanide with colors obtained from oils containing known percentages of sulfur, it gave a color corresponding to less than 0.01 per cent.<sup>1</sup> Inasmuch as petroleum dissolves sulfur to the extent of 3 per cent there are probably few crude oils

that do not contain this element or its hydrocarbon derivatives. A wide range of crude oils tested by this method all gave colors for sulfur except such light varieties as those from Pennsylvania, West Virginia and the Berea Grit oils of southern Ohio, all of which consists very largely of the series  $C_nH_{2n+2}$ , including the solid paraffine hydrocarbons, none of which showed a trace of sulfur.

Nitrogen is a significant element relating to the formation of petroleum, since it has been assumed that nitrogen compounds in petroleum could have had their source only in organic matter of animal origin. In most varieties of American petroleum nitrogen has been identified—to the largest extent in California oils. It therefore seemed interesting to ascertain whether Mahone petroleum contains nitrogen: 5 grams of the oil were subjected to the Kjeldahl method with the precaution necessary to convert all the nitrogen of the possible pyridine or choline compounds into ammonia, and the resulting solution distilled, and Nesslerized. No trace of color appeared, thus excluding nitrogen as a constituent. A specimen of Pennsylvania petroleum tested in the same way gave not a trace of nitrogen as ammonia. The question as to the presence of nitrogen in other varieties of American petroleum will be determined in this manner.

Mahone petroleum is unique in composition in that it contains no hydrocarbon of the series  $C_nH_{2n+2}$ , gasoline or kerosene, and none of the series  $C_nH_{2n}$  that constitutes so large a proportion of Pennsylvania lubricants. So far as it can be distilled *in vacuo* this oil consists very largely if not entirely of the series  $C_nH_{2n-2}$ , and the series  $C_nH_{2n-4}$ . As to the composition of the residue of distillation above 350° under 30 mm. pressure nothing can be said, for at this point or perhaps somewhat lower in temperature the hydrocarbons simply fall asunder, having reached the limit of their capacity to maintain molecular composition, and the distillates come over as thinner oils. These changes are readily and accurately detected by the viscosity and cold tests of the distillates which without warning may change in viscosity from 250 to less than 100, and the cold test from -20 to +10°. Under atmospheric pressure the crude oil begins to distil at 230°, and at 250° it begins to decompose, breaking down into thinner oils. It will be interesting to ascertain the composition of these products of decomposition. If the distillation be continued beyond this point, the residue consists of a thin tar which, *in vacuo*, may be run down to within two per cent of residue without coking. The general distinction of the varieties of petroleum, those with a paraffine base and those with an asphaltic base, does not apply to Mahone petroleum, which contains neither paraffine nor the so-called asphaltic hydrocarbons. While the crude oil contains no crystalline hydrocarbons (at least none were observed at a temperature of -20°) when decomposition is caused by distillation, crystalline hydrocarbons appear in the residue, and in the higher distillates. There is a close connection between the formation of these

<sup>1</sup> This is an extremely delicate test for sulfur in petroleum oils, and extremely accurate quantitatively based on the comparative depths of color given by oils with 0.1, 0.01, and 0.001 percentages as standards.



crystalline bodies and changes in the cold test. These changes are directly the opposite of those which occur under similar conditions in other petroleum with the tendency is toward a breaking down of the crystalline hydrocarbons into thin oils. Nevertheless the hydrocarbons in Mahone petroleum are remarkably stable in distillation when air is excluded and under diminished pressure. Distillates prepared in the course of this work were carried apparently unchanged as shown by analysis through fourteen repetitions, and as it seemed, the distillations could have been continued indefinitely without decomposition.

Determinations of carbon and hydrogen in the crude oil gave percentages corresponding to the series  $C_nH_{2n-2}$ : C, 86.42; H, 13.31. Assuming a mean composition represented by the formula  $C_{20}H_{38}$ , the proportions of carbon and hydrogen are: C, 86.33; H, 13.67. To separate the constituents of the crude oil, so far as it can be done by distillation *in vacuo* without decomposition, the light and heavy fractions from five gallons, separated first in iron stills, were carried through a prolonged series of distillations and finally collected within limits of single degrees under 30 mm. The lowest fraction came over in the vicinity of 90° and in quantity only 15 grams. Its odor resembled that of the terpenes—quite unlike the odors of the petroleum hydrocarbons. A somewhat larger amount, 35 grams, collected after the twelfth distillation at 97°–98°. Fractions also collected in much larger amounts at quite regular intervals of 10° as the distillation proceeded, as follows: 109°–110°, 40 grams; 120°–121°, 79 grams; 130°–131°, 143 grams; 138°–139°, 207 grams; 151°–152°, 300 grams; 161°–162°, 425 grams; 171°–172°, 500 grams. At higher temperatures there was still a tendency for quantities to accumulate but at somewhat longer limits, 15°. Hitherto, good evidence of the series  $C_nH_{2n-2}$ , and  $C_nH_{2n-4}$  in petroleum has been obtained in this laboratory, but the results herewith presented are conclusive and more comprehensive. The series in Mahone petroleum is defined by analysis, and the individual hydrocarbons by determinations of their molecular weights, which gave very satisfactory results by reason of the prolonged distillations on which an assistant was engaged nearly all his time during twelve months. All molecular weights were determined by the Beckmann freezing-point method.

The fraction 97°–98° was examined with considerable interest, for if any hydrocarbon of the series  $C_nH_{2n}$  were present in the crude oil it should appear at this point. But its molecular weight was found to be 153; calculated for the formula  $C_{11}H_{20}$ , 152; specific gravity at 20°, 0.8549. A combustion gave percentages required for the same formula: Carbon, 86.76; Hydrogen, 13.26; required for  $C_{11}H_{20}$ : Carbon, 86.84; Hydrogen, 13.26. It is, therefore, safe to conclude that the series  $C_nH_{2n}$  is not present in this petroleum. The fraction collected at 109°–110° gave as its specific gravity at 20°, 0.8576, and as its molecular weight, 166; required for the formula  $C_{12}H_{22}$ , 166. A combustion gave:

Carbon, 86.49; Hydrogen, 13.44; required for the formula  $C_{12}H_{22}$ : Carbon, 86.74; Hydrogen, 13.26.

Hydrocarbons of this series with such low molecular weights have not hitherto been separated from petroleum. A hydrocarbon,  $C_{13}H_{24}$ , was identified in this laboratory as a constituent of Santa Barbara, Cal., petroleum, and several of the same series with much higher molecular weights from Ohio and Pennsylvania oils as constituents of lubricants prepared from these oils.

The composition of the fraction 120°–121° was shown by its molecular weight, 180.4; required for the formula  $C_{13}H_{24}$ , 180, and by combustion: Carbon, 86.72; Hydrogen, 13.33; required: Carbon, 86.66; Hydrogen, 13.34; specific gravity, 0.8614. Since the hydrocarbon separated from Santa Barbara oil was collected under 60 mm. and none of that product is still on hand, it cannot be compared with the one now under examination.

The molecular weight of the fraction 130°–131° was found to be 194; required for  $C_{14}H_{26}$ , 194. By combustion it gave: Carbon, 86.48; Hydrogen, 13.64; required: Carbon, 86.60; Hydrogen, 13.40; specific gravity at 20°, 0.8654.

A molecular weight determination of the fraction 138°–139° gave 206.7; required for  $C_{15}H_{28}$ , 208. It gave by combustion: Carbon, 86.38; Hydrogen, 13.64; required for  $C_{15}H_{28}$ : Carbon, 86.54; Hydrogen, 13.46; specific gravity at 20°, 0.8662. The fraction 151°–152° gave as its molecular weight, 218.7; required for the formula  $C_{16}H_{30}$ , 218. It gave by combustion the following percentages of carbon and hydrogen: Carbon, 87.07; Hydrogen, 12.88; required: Carbon, 87.28; Hydrogen, 12.72; specific gravity at 20°, 0.8692.

For the fraction 171°–172° was found the molecular weight 235; required for the formula  $C_{17}H_{30}$ , 234. A combustion gave the following percentages of carbon and hydrogen: Carbon, 87.02; Hydrogen, 12.90; required for  $C_{17}H_{30}$ : Carbon, 87.18; Hydrogen, 12.82; specific gravity at 20°, 0.8716. Of the higher fractions to be more fully examined later, that collected at 212°–214° gave as its molecular weight 263; corresponding to the formula  $C_{19}H_{34}$ , molecular weight 262. It gave, by combustion, percentages of carbon and hydrogen required by this formula: Carbon, 87.12; Hydrogen, 13.01; required for  $C_{19}H_{34}$ : Carbon, 87.03; Hydrogen, 12.97; specific gravity at 20°, 0.8790. The series  $C_nH_{2n-4}$  is, therefore, established as constituting much the larger part of Mahone petroleum so far as this examination extended. It appears also that as commercial products lubricants may be prepared from this crude oil that shall contain four hydrocarbons, and even only two, of this single series. This applies likewise to Texas petroleum since it has been found in this laboratory that the most valuable lubricants separated from that crude oil are composed of hydrocarbons of this series,  $C_nH_{2n-4}$ , as has also been shown for lubricants prepared from California petroleum.

These results are summarized in the following table:

Dis- tillation tempera- ture	Actual determination				Required			
	p	wt.	C	H	for	Mol.	C	H
97°-98°	0.8549	153	86.76	13.26	C <sub>10</sub> H <sub>20</sub>	152	86.84	13.16
109°-110°	0.8576	166	86.49	13.51	C <sub>11</sub> H <sub>22</sub>	166	86.74	13.26
120°-121°	0.8614	180.4	86.72	13.23	C <sub>12</sub> H <sub>24</sub>	180	86.66	13.34
130°-131°	0.8654	194	86.48	13.64	C <sub>13</sub> H <sub>26</sub>	194	86.60	13.40
138°-139°	0.8690	206.7	86.38	13.64	C <sub>14</sub> H <sub>28</sub>	208	86.54	13.46
151°-152°	0.8692	218.7	87.07	12.88	C <sub>15</sub> H <sub>30</sub>	218	87.28	12.72
171°-172°	0.8716	235	87.02	12.90	C <sub>16</sub> H <sub>32</sub>	234	87.18	12.02
211°-214°	0.8790	265	87.10	13.01	C <sub>17</sub> H <sub>34</sub>	262	87.03	12.97

The higher fractions will be more fully examined later.

#### INDEX OF REFRACTION

Three specimens of the crude oil collected in different years and from different wells gave the following indices of refraction in an Abbé refractometer at 26°:

I	II	III
1.4878	1.4878	1.4882

Fractions obtained by prolonged distillation as described above gave the following indices:

80°-81°	1.4490
97°-98°	1.4570
120°-121°	1.4625
138°-139°	1.4645
151°-152°	1.4688
230°-265°	1.4820
265°-115°	1.4879

These results were obtained after treatment with sulfuric acid; the indices were the same before and after this treatment.

#### ORIGIN OF MAHONE PETROLEUM

The question of the origin of petroleum has received profound attention both from geologists and chemists, but it is yet elusive on account of the difficulty of securing reliable data that should explain the conditions under which it was formed, and of accounting for the several series of hydrocarbons of which it is composed. Then, further, the absence of organic material as a possible source, and the geological disturbances associated with its present situation afford too meager information for its complete elucidation. In the petroleum under consideration several of these uncertain features were eliminated. In the first place, the shallow depths of the oil strata and its apparent common origin from vegetation with the extensive beds of coal close at hand indicate a more recent formation of these oil deposits than can be assigned to other well known varieties that occur at greater depths. In the Mahone field, the oil sand has evidently not been disturbed since the oil was therein accumulated. The neighboring coal strata suggested a coincident formation of the oil as an intermediary product between vegetation and coal and that subsequent geological conditions of heat and pressure forced out the liquid hydrocarbons forming the oil deposits as they now appear. This view of its origin is supported by recent experimental evidence. Pictet and Bouvier<sup>1</sup> distilled Montrambert (Loire) coal under 15-17 mm. pressure, and fractionated the tar. They isolated two hydrocarbons, C<sub>15</sub>H<sub>30</sub> and C<sub>17</sub>H<sub>34</sub>, which they found to be identical with hydrocarbons separated from Cana-

dian petroleum. After giving the closely agreeing values as to specific gravity, molecular weights, and refractive indices, they summarized the comparison as follows:

"Vergleicht man nun die von Mabery angegebenen Eigenschaften dieser beiden Fraktionen mit denen unserer Kohlenwasserstoffe C<sub>15</sub>H<sub>30</sub> und C<sub>17</sub>H<sub>34</sub> aus dem Vakuumteer, so sieht man, dass sie sich ebenfalls fast genau decken. Die Uebereinstimmung ist eine so gute, dass man daran nicht zweifeln kann, dass es sich nicht mehr um isomere, sondern um identische Körper handelt, und dass im canadischen Petroleum und im Vakuumteer der Steinkohle von Montrambert dieselben Kohlenwasserstoffe C<sub>15</sub>H<sub>30</sub> und C<sub>17</sub>H<sub>34</sub> vorhanden sind. Mit andren Worten werden durch Vakuumdestillation gewisser Steinkohlen Körper gewonnen, die sich anderswo als Bestandteile gewisser Erdole vorfinden. Somit ist zum ersten Mal ein chemischer Zusammenhang zwischen den beiden Naturprodukten auf experimentellen Wege dargetan."

The last important statement may be translated as follows:

Therewith for the first time is a chemical connection between both these natural products (coal and petroleum) established by experiment.

The complete absence of the series C<sub>n</sub>H<sub>2n+2</sub> is not unusual; those hydrocarbons are wanting in most heavy varieties, but the series C<sub>n</sub>H<sub>2n</sub> is more frequently present. In composition, Mahone petroleum evidently stands between varieties with the so-called paraffine base, such as Pennsylvania and Ohio on the one hand, and those with an asphaltic base such as the Texas and California varieties on the other. The absence of paraffine is significant since it shows that the oil as originally formed has all been converted into series with less hydrogen. Likewise the absence of asphaltic constituents is significant as indicating that the changes in formation have not been such as to include these bodies poorer in hydrogen, either through the agency of heat or pressure, or by the prolonged action of sulfur on the atmosphere, which no doubt are concerned with the formation of natural asphalts.

The determining influence of sulfur and oxygen in the primary formation of the principal constituents of petroleum evidently cannot be disregarded in attempting to account for their origin. As mentioned above, the heavy varieties of petroleum dissolve sulfur to the extent of three per cent of their weight. I found that one variety of Texas oil, the "Humble Crude," contained three per cent of sulfur, the greater part as the element in mechanical solution. Much the larger proportion of the world's supply of petroleum contains sulfur in considerable quantities, in part, in the form of hydrocarbon derivatives, such, for example, as compounds of the series C<sub>n</sub>H<sub>2n</sub>S which were identified in this laboratory as constituents of Ohio, Indiana, and Canadian petroleum.

In a paper published several years ago I expressed the opinion which was quoted by Engler in "Das Erdöl," that petroleum containing sulfur probably had its source in organic remains of animal origin. But more recent study of the relations of sulfur and petro-

<sup>1</sup> Ber. d. chem. Ges., Nov., 1903, 333.

leum hydrocarbons especially in connection with crude oils from the Texas fields makes it plain that any petroleum may contain sulfur whatever its origin, provided it comes in contact with native sulfur which is widely distributed.

As is well known any hydrocarbon heated with sulfur loses hydrogen and evolves  $H_2S$ ; if the hydrocarbon be of the series  $C_nH_{2n+2}$  it is pretty certain under carefully regulated conditions that the hydrocarbon nucleus will combine with more of the sulfur but this feature of its action has not been fully verified. In the study of the hydrocarbons distilled from coal by Pictet and Bouvier it was found that  $H_2S$  was evolved when the hydrocarbons were heated with sulfur and that sulfur derivatives were formed. On account of the instability of the sulfur derivatives of the hydrocarbons, unless special care is exercised, it is probable that the principal products should be hydrocarbons poorer in hydrogen, such as the series  $C_nH_{2n}$ ,  $C_nH_{2n-2}$ ,  $C_nH_{2n-4}$ , that constitute the main body of petroleum. The formation of the great quantities of hydrogen sulfide that escape from many oil wells takes place freely under the influence of heat and pressure; it may be by simple contact under pressure in long geological periods. Experimentally by prolonged heating with sulfur the lighter hydrocarbons may be converted into solid asphalts.

All natural asphalts contain sulfur to a greater or less extent, and in view of its ready action on the hydrocarbons it is safe to conclude that it has had much to do with their formation. What most impresses a visitor to the great asphalt lake on the Island of Trinidad, is the question as to its formation. On observing close at hand, however, numerous petroleum wells with a large output, and bearing in mind the large amounts of sulfur contained in these immense beds of semi-solid bitumen, the answer is not far to seek.

The instability of the petroleum hydrocarbons in presence of air is a matter of common observation in the manipulation of crude oil and its products. In lighter refined oils on standing color reappears. During distillation the heavier constituents increase in gravity, finally forming asphaltic residuum and coke. The difficulties arising from this influence of oxygen are the most perplexing of all that beset the arduous duties of the refiner. This action of oxygen on the hydrocarbons is taken advantage of in the Byerley process for the conversion of residuum into hard asphalts by passing air through the residuum at carefully regulated temperatures. Evidently all changes of this nature with oxygen as with sulfur depend on the abstraction of hydrogen; it is doubtful whether under these conditions oxygen enters at all into combination with the hydrocarbon nucleus.

While a full explanation of the origin of petroleum should include a plausible source of all its constituents, sulfur and nitrogen derivatives, phenols, acids, and aromatic hydrocarbons, the fundamental demand is for a clear statement based on experimental data concerning the principal series of hydrocarbons. The unquestionable source of the petroleum hydrocarbons is organic remains either of vegetable or animal origin,

it matters little which, for either is experimentally known to yield hydrocarbons by decomposition. In one section of oil territory it may have been the enormous growth of the carboniferous age that gave the coal; in other sections it may have been the extensive beds of sea weeds, and in still another the organic remains of the great masses of shells that have formed the limestones and dolomites.

Reichenbach was the first to recognize the presence of paraffine in the products of decomposition of organic matter, and it has since been frequently obtained with its lower congeners from various animal and vegetable sources. Breaking down of paraffine into lower members of the same series under the influence of heat and pressure was observed by Thorpe, and no doubt this experimental formation is a close duplicate of similar changes produced in long periods of time under natural agencies. Even when heated with exposure to air, paraffine gradually breaks down to lower hydrocarbons. It is certain that these changes are not possible in the reverse order, that is, the production of paraffine from lower hydrocarbons. In such molecular decompositions by a simple break in the hydrocarbon chain, a paraffine hydrocarbon, for example,  $C_{25}H_{52}$ , should give one  $C_{12}H_{26}$ , and one  $C_{13}H_{28}$ , or by simple loss of hydrogen it should give  $C_{25}H_{46}$  of the series  $C_nH_{2n-4}$ . Evidently in such decompositions other bodies are formed even proceeding as far as marsh gas. A great variety of such changes are experimentally possible especially with the aid of sulfur or atmospheric oxygen, and in the earth with the aid of natural heat and pressure, yielding as final products the asphalts, or proceeding directly from vegetation to the beds of coal. These changes together with possible evaporation doubtless explain why the series  $C_nH_{2n+2}$  is not found in the heavier varieties of petroleum.

In studying the characteristics of these series as they appear in extended distillation up to the breaking point, together with their behavior toward oxygen and sulfur, one can hardly escape the conviction that the hydrocarbons which constitute the main body of all varieties of petroleum have been formed from organic matter in nature's laboratory by these progressive changes. Certainly any attempt to account for the origin of petroleum must be based on its composition which includes principally the series of hydrocarbons above mentioned, and the fact that changes in composition are always in the direction of the lower series and lower members, with loss of hydrogen.

In the origin of Mañone petroleum the influence of sulfur was precluded, for the oil is practically free from this element. By reason of the shallow depths of the porous strata, contact with air was possible with its influence in removing hydrogen, but this action did not continue beyond the formation of the few series of hydrocarbons which the crude oil contains, since the oil is free from the asphaltic hydrocarbons. These porous conditions were likewise favorable for the escape of the hydrocarbons  $C_nH_{2n+2}$  and  $C_nH_{2n}$ . Its proximity to the coal, its shallow occurrence, and the experimental results of Pictet and Bouvier are pretty conclusive evidence that the oil was exuded from the



coal doubtless long subsequent to its formation, and perhaps with later changes in composition. This connection between Mahone petroleum and the neighboring coal will receive further attention in this laboratory, together with the products of distillation of the natural asphalts.

On account of the simple composition of Mahone petroleum and its freedom from deteriorating bodies it is especially adapted for the preparation of superior lubricants. In the absence of gasoline and kerosene hydrocarbons, paraffine or other crystalline bodies, with due precautions, distillates may be obtained with extremely low cold tests. So long as the hydrocarbons  $C_nH_{2n-4}$  remain intact they constitute the most durable body in lubrication that it is possible to prepare from petroleum. The lighter hydrocarbons of the series  $C_nH_{2n-2}$  with lower viscosity,  $100^\circ$  to  $125^\circ$ , have similar qualities. This petroleum, therefore, yields a range of lubricants especially adapted for delicate mechanism from a chronometer to a sewing machine, and they are widely in use as prepared by the Eagle Lubricant Manufacturing Company.

With reference to the formation of petroleum in general, no additional evidence concerning its geological occurrence has been forthcoming within recent years. More extended knowledge as to its composition and the relations of its constituents have an important bearing on its origin. All published results and opinions bearing on the chemical aspects of its origin were recently thoroughly reviewed by Engler ("Das Erdöl", Leipsic, 1912). The theory of its formation from carbides, suggested by Mendeleff and more forcibly presented by Moissan and accepted ten years ago as a plausible theory, is now generally considered as involving too many hypotheses and subsequent changes. Earlier views of the transportation or migration of petroleum from the place of its origin to other strata are no longer generally accepted. Filtration was possible of the thinner varieties. That Ohio and Indiana petroleum was formed from the remains of shell fish coincident with the formation of its Trenton limestone habitat as ably maintained by Orton admits of no other explanation. The same may be said of Hunt's views as to the formation of petroleum in the Corniferous limestone.

Under the term bitumen is included natural gas, petroleum, natural asphalts, and coal—the "organoids" (Engler)—with a closer similarity between the members of the group than has been hitherto admitted, especially in their primal evolution. It seems evident that the formation from vegetation of Pennsylvania petroleum as well as of other similar oils which consist mainly of the hydrocarbons  $C_nH_{2n+2}$ , was accompanied by less chemical change than that of other varieties. The vegetable matter first gave paraffine as the principal product, which by natural agencies broke down into lower hydrocarbons. Then Pennsylvania petroleum was not subject to the action of sulfur which has been evidently an active agent in the formation of the heavier varieties.

Between the Pennsylvania type of petroleum and the asphalts and coals there are all stages of variation

in composition resulting from the greater or less chemical changes in the primary series of hydrocarbons. Since sulfur is associated with all the heavier varieties of oil, asphalts, and coal, as well as a part of their composition, from what is known concerning its action on the hydrocarbons, it is difficult to escape the conviction that this element was largely instrumental in forming the series of hydrocarbons poorer in hydrogen that constitute the principal body of all these natural products. Only a moderate increase in temperature is necessary for its action, and such temperatures are quite sufficient to account for the loss of hydrogen even to carbonization as in the formation of coal. But since in the coals are still to be found petroleum hydrocarbons, the similar origin of coal and at least some varieties of petroleum is evident. Unquestionably the vast deposits of oil in Texas were formed in a manner analogous to those in Pennsylvania, probably from vegetable matter and that through their association with extensive beds of sulfur, the series  $C_nH_{2n+2}$  disappeared completely by conversion into the series with less hydrogen including the asphaltic hydrocarbons.

In the immense fields of California of more recent origin where the oil contains large proportions of nitrogen and sulfur compounds, aromatic hydrocarbons, and an exceptionally large proportion of asphaltic bodies, there is good evidence of the action of sulfur. With reference to the large amount of nitrogen compounds contained in California petroleum, they could evidently have been formed from vegetation and their presence may be explained by their recent origin of which there is undoubted evidence in some of the California fields. That the older oil deposits in Pennsylvania and Texas contain only very small proportions of nitrogen compounds, may have resulted from the breaking up of these compounds and their disappearance in the longer periods of time. The swarming maggots that have been observed in some California petroleum are doubtless the result of bacterial action on the products of decayed vegetation. It, therefore, seems evident that the origin of California petroleum must also be looked for chiefly, if not entirely, in the decay of vegetation and that the hydrocarbons of which California oil now consists were formed primarily from the series  $C_nH_{2n+2}$  by loss of hydrogen.

At any rate, whatever conclusion is reached as to the source of the bitumens, it must be in accordance with the predominating characteristic of the hydrocarbons to lose hydrogen and to break down from those most highly hydrogenized through lower series to the asphalts and even to coal. It should also account for a closer relationship in origin between the deposits of coal, asphalts and petroleum than has hitherto been recognized.

While these views are evidently in some respects at variance with those formerly expressed, if as it seems plain, the origin of petroleum as well as of the other bitumens, is to be explained more directly on the basis of its composition, and the chemical changes to which it has been subjected in, and since, its evolution from organic matter, the question as to its history is

divested of many complicating assumptions, and greatly simplified.

I should acknowledge my obligations to Mr. James Graham for assistance in the experimental work of this paper.

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### THE PREPARATION OF METALLIC COBALT BY REDUCTION OF THE OXIDE<sup>1</sup>

By HERBERT T. KALMUS

In connection with the work on cobalt it has been necessary to prepare considerable quantities of the metal in as pure a state as possible. Nearly 1000 pounds of commercial black cobalt oxide have been given to this laboratory for these researches by the Deloro Mining and Reduction Co. of Deloro, Ontario, to whom we take this opportunity of expressing our thanks.

The writer wishes to acknowledge the work of Messrs. C. Harper, W. L. Savell, C. W. Day and R. Wilcox, who, in the capacity of research assistants at these laboratories, have done most of the actual experimenting. To Professor S. F. Kirkpatrick of the Department of Metallurgy, Queen's University, thanks are due for many valuable suggestions.

The process for the preparation of fairly pure cobalt oxide has been very completely worked out, and has been practised on a large scale at several Canadian smelters. For this reason the oxide was chosen as a raw material from which to prepare the metal. As the work progressed, it became more and more apparent that some of the uses for cobalt which were being demonstrated at these laboratories and elsewhere, would lead to the preparation of the metal in large quantities. Hence, it became of increasing importance that the metallurgy of the preparation of the metal from the oxide be studied, and this has been done with greater care than was necessary merely for the production of the quantities required for experimental purposes. There are four important reducing agents for obtaining metallic cobalt in reasonably pure form from commercial cobalt oxide. They are: I, Carbon; II, Hydrogen; III, Carbon Monoxide; IV, Aluminum.

The  $\text{Co}_3\text{O}_4$  used<sup>2</sup> for these experiments was made from cobalt hydrate, precipitated by bleach from a cobalt chloride solution. This hydrate, in contact with the atmosphere, is greenish black in color. It was calcined at  $750^\circ\text{C}$ , yielding a black oxide of approximately the composition  $\text{Co}_3\text{O}_4$ . This is shown by the following analyses, made at widely different times, which are typical of a large number:

#### ANALYSES OF PURIFIED COBALT OXIDE (PERCENTAGES)

	June, 1912	November, 1912	April, 1913
Co.....	71.99	71.52	72.3
Fe.....	0.11	0.27	0.10
Ni.....	0.040	0.020	Trace
S.....	0.020	Trace	0.052
Ca.....	0.030	...	0.15
SiO <sub>2</sub> .....	0.19	0.13	0.39

The oxides corresponding with the theoretical formulas would have cobalt content as follows:

Formula	Percentage, cobalt
$\text{Co}_2\text{O}_3$ .....	71.1
$\text{Co}_3\text{O}_4$ .....	73.4
$\text{CoO}$ .....	76.0
$\text{Co}_2\text{O}$ .....	78.8

It is obvious then, when we take into account the portion of the sample which is not cobalt oxide, that the oxide itself is largely  $\text{Co}_3\text{O}_4$ . It is not necessary for the purpose of our calculations to assume that this oxide alone is present, for we shall base our computations upon the actual analyses as we have found them. However, in writing the reactions throughout this paper, we shall, for simplicity, consider the oxide to be  $\text{Co}_3\text{O}_4$ .

#### PURIFICATION OF COBALT OXIDE

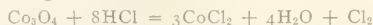
Cobalt oxide as we obtained it from the smelters, and as sold on the market, analyzed approximately as follows:

Barrel 1	Percentages	Barrels 3 and 4	Percentages
Co.....	70.36	Co.....	69.2
Ni.....	1.12	Ni.....	1.4
Fe.....	0.82	Fe.....	0.50
S.....	0.45	CaO.....	0.37
As.....	0.10	S.....	0.54
SiO.....	0.20	Insoluble.....	1.46
Ca.....	0.50	Ag.....	Trace

Analyses, of course, vary considerably from one shipment to another; the above samples are high in Fe, S and Ca, and would be considered by most smelters as No. 2 grade.

Metal produced from oxide analyzing as above, by the method to be described, is of sufficient purity for most purposes. This is especially true if lime be added to the melt to slag off the sulfur. However, for other purposes metal is required in which the impurities, nickel, iron, sulfur, arsenic and silica, are reduced to very small percentages. In this case it is best to remove these impurities from the oxide before reduction. Starting with a crude cobalt oxide, these impurities may be reduced as far as is desired by the following procedure:

**SILICA**—Dissolve the crude oxide in hydrochloric acid according to the reaction:



This may be done best by heating and agitating with steam. If silica is present, it will not dissolve, and may be removed by filtration or decantation. The same is true of silicates which are not decomposed by this treatment. Decomposable silicates would send a certain amount of silica into solution, which would be thrown out during the next step.

**IRON AND ARSENIC**—To the cobalt chloride solution formed by dissolving the oxide in hydrochloric acid,

<sup>1</sup> Author's abstract of report under the above title to the Canadian Department of Mines. Published by permission of the Director of Mines, Ottawa, Canada. The general investigation of the metal cobalt and its alloys, with reference to finding increased commercial usages for them is being conducted at the School of Mining, Queen's University, Kingston, Ontario, for the Mines Branch, Canada Department of Mines.

<sup>2</sup> For a consideration of the various oxides of cobalt, including the proof that the black oxide used for these reductions was largely  $\text{Co}_3\text{O}_4$ , see the following article, page 115.

gradually add finely divided  $\text{CaCO}_3$  or pure marble, until no further precipitate is formed. The heavy brown mud precipitated contains the iron and arsenic content of the original oxide.

**NICKEL**—For most purposes it will not be necessary to separate the small amount of nickel from the cobalt, but it may be done as follows: The cobalt chloride solution, containing a certain amount of nickel chloride, is of an intense red or claret color. Add a solution of bleach to the solution until it has almost completely lost its color. The bleach solution differentially precipitates hydrates of nickel and cobalt, so that the nickel is not appreciably brought down until the cobalt has been almost entirely precipitated.

The bleach will precipitate a black hydrated oxide of cobalt, and the diminishing redness of the solution will indicate the end point. If all of the steps above outlined have been applied to the original oxide, this final black precipitate may be calcined at about  $750^\circ \text{C.}$ , to yield black  $\text{Co}_3\text{O}_4$ .

**SULFUR**—Any sulfur present in the original oxide and carried through to the final product, or introduced with the bleach, may be removed by boiling the final dried oxide with sodium carbonate and dilute hydrochloric acid. The reaction is:



The soluble sodium sulfate formed is washed out with water. A further washing is given with dilute hydrochloric acid, which decomposes the calcium carbonate into soluble calcium chloride and  $\text{CO}_2$  gas. The  $\text{CaCl}_2$  is washed out with water. This method is, of course, applicable only for the removal of the small percentages of Ca and S found in the oxides in question.

A shipment of oxide from the smelter was analyzed before and after treatment by the above method, with the following results:

Percentages	Before	After
Co.....	70.36	71.99
Ni.....	1.12	0.041
Fe.....	0.82	0.11
S.....	0.45	0.020
Ca.....	0.50	0.021
As.....	0.10	None
SiO <sub>2</sub> .....	0.20	None

There are other obvious methods of purifying the  $\text{Co}_3\text{O}_4$ . For example, the bleach solution may be freed of its  $\text{SO}_4$  content with  $\text{BaCl}_2$ , and the Ca and excess Ba precipitated with  $\text{Na}_2\text{CO}_3$ , thus yielding a fairly pure solution of soda bleach. The  $\text{SO}_4$  content of the  $\text{CoCl}_2$  solution may be precipitated with  $\text{BaCl}_2$  and the differential precipitation of cobalt and nickel accomplished with the purified solution of soda bleach.

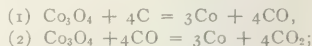
#### I—REDUCTION OF COBALT OXIDE WITH CARBON

**METHOD OF EXPERIMENT**—These experiments all consisted in intimately mixing definite amounts of finely divided carbon in various forms with  $\text{Co}_3\text{O}_4$ , and heating the mixture to constant temperature for a measured time. The charges employed varied in size from a few grams to 10 lbs., and were heated in lined and unlined graphite crucibles, and in porcelain crucibles.

**FURNACES**—The reduction took place either in an

oil-fired "Steele-Harvey" furnace of 60 pounds, metal capacity, No. 20 crucible, which could be controlled at any temperature up to  $1550^\circ \text{C.}$ , or in a modified Hoskins electric resistor furnace. This latter has a heating chamber, 8 inches cube, which can be maintained constant to within about  $10\text{--}20^\circ \text{C.}$ , at any temperature up to  $1650^\circ \text{C.}$  Some of the small charges were run in porcelain crucibles heated within an electric resistor furnace.

The reactions for the reduction of cobalt oxide with carbon are:



or, combining (3)  $2\text{Co}_3\text{O}_4 + 4\text{C} = 6\text{Co} + 4\text{CO}_2$ .

If all the oxygen for the oxidation of the carbon be supplied by the cobalt oxide, and if all the carbon be burned to  $\text{CO}_2$  then the reaction goes according to the last equation.

In practice, neither of these conditions is strictly obtained, but with proper design of furnace they may be closely approximated.

**THE RUN**—In each case the charge was made up by intimately mixing a weighed amount of finely divided oxide with a weighed amount of finely ground carbon. This mixture was placed in the crucible, which, with its charge, was placed either in the Steele-Harvey oil furnace or in the electric furnace. The mixture was frequently stirred with an iron rod during the reduction.

**THE CARBON**—The form of carbon chosen for the reduction, whether powdered charcoal, coke, coal, etc., depends somewhat upon the impurities from which it is desirable to keep the resulting metal free, but also this choice greatly influences the speed of the reduction.

Three sets of experiments were made with powdered anthracite coal, while further runs were made with lamplblack or with powdered charcoal. The carbon was in all cases powdered to an extremely fine flour.

**TEMPERATURE MEASUREMENTS**—Temperature readings were made at frequent intervals with a platinum platinum-rhodium thermo-element, with a Wanner optical pyrometer, or with a F ry radiation pyrometer, and the furnace adjusted to keep the temperature constant to within about  $20^\circ$ .

The charge was put into the crucible which was within the furnace, both crucible and furnace being at a temperature somewhat higher than the intended temperature of the run. Some of the smallest charges were inserted with containing crucible. It was learned, by experience, for the different sizes of charge and qualities of crucible, at about what temperature to maintain the furnace prior to inserting the charge, in order that the charge might come to the desired equilibrium temperature, with proper furnace adjustment, in about ten minutes. There is, therefore, a period of about ten minutes, at the beginning of each run, during which the average temperature of the charge is not as high as that noted with the Wanner optical pyrometer, which observes the surface of the charge. We satisfied ourselves that the center of the charge was at the same temperature as the surface, within  $20$  or  $30^\circ \text{C.}$ , after the first ten minutes, by exploring the center with a thermo-element, and noting simul-



taneously its readings and those of another thermo-element near the surface, and of the Wanner optical pyrometer.

In the following runs we have not attempted to make a correction for the lag in coming to temperature during these first ten minutes. This lag would be considerably less than ten minutes for the smallest crucibles used, about ten minutes for the four-pound charges, and possibly as long as twenty minutes in the worst cases, with the ten-pound charges.

The oxides used for the runs reported in Tables I and II analyzed as follows:

Runs	Percentages	
	A-H	RI-VIII
Co	71.36	69.2
Ni	1.12	1.4
Fe	0.82	0.50
S	0.45	0.54
Ca	0.50	CaO..... 0.37
As	0.10	Insoluble 1.46
SiO <sub>2</sub>	0.20	Ag Trace

The anthracite coal used was very finely powdered. In the typical runs A-H, No. 12 unlined carbon crucibles were used, and the charge was stirred every ten minutes during reduction. In these runs no

TABLE I—REDUCTION OF  $\text{Co}_3\text{O}_4$  WITH POWDERED ANTHRACITE COAL (A)  
RUNS A, C, H—HARVEY-STEEL OIL FURNACE  
G, B, D, E, F—ELECTRIC CRUCIBLE FURNACE

No. of run	Charge		Average temperature °C.	Time of reduction Min.	Yield of cobalt	
	Co <sub>3</sub> O <sub>4</sub> Lbs.	Coal Oz.			Lb. Oz.	Per cent of theoretical
A.....	5	8.3	1200	90	3 1.5	87
C.....	4	6.9	1200	30	2 12.5	98
H.....	10	16.0	1200	105	6 9	92
G.....	4	6.6	900	150	2 13	99
B.....	4	6.54	1200	60	2 13	99
D.....	4	6.9	1200	120	2 13.5	100
E.....	4	6.9	1500	60	2 11.75	96
F.....	4	6.6	1500	90	2 12.7	98

A—Considerable unreduced oxide slag. Carbon used is approximately the theoretical amount according to reaction (3).

C Melt free from unreducible oxide slag. Carbon 10 per cent in excess of theoretical requirement.

H—3 oz. lime added shortly before pouring. Carbon, theoretical amount.

G—At end of 2.5 hours, charge not completely reduced, but completed during subsequent raising to melting point.

TABLE II—REDUCTION OF  $\text{Co}_3\text{O}_4$  WITH POWDERED ANTHRACITE COAL (B)  
HARVEY-STEEL OIL FURNACE

No. of run	Charge		Average temp. °C.	Reduction time to removal of sample Minutes	Per cent	
	Co <sub>3</sub> O <sub>4</sub> Lbs.	Coal Oz.			Co in sample (a)	Reduction complete = 100
I....	10	17.5	601	R2 82	73.6	Very slight
II....	10	16.5	750	R3b 91	74.1	Very slight
III....	10	16.5	888	R4b 90	73.8	Very slight
IV....	10	16.5	1057	R5b 95	80.8	28
VI....	10	16.5	1203	R6a 30	81.3	30
				R6b 49	93.0	74
VII....	10	16.5	1283	R7a 31	91.1	70
				R7b 47	93.9	77
VIII....	10	17.4	1502	1 11	76.7	12
				2 16	81.8	32
				3 21	91.0	66
				4 26	93.9	77
				5 31	93.9	Apparently some oxidation
				6 36	91.8	oxidation

(a) These analyses are for cobalt, nickel and iron combined, of which about 97 per cent was cobalt, as may be seen from the analysis of the original oxide. Carbon analyses were of course made, and the percentage of cobalt given in this column takes into account the residual carbon.

attempt was made to show the progress of the reduction, but at the close of the run the charge was raised as rapidly as possible to the melting point and the melt poured into an iron mould to be weighed. Considerable reduction must take place during the interval of melting the charge after the close of the run. The purpose of these particular runs was to study the yields under somewhat the same conditions which must necessarily obtain in practice. In the runs I-VIII, No. 20 unlined carbon crucibles were used; no attempt was made to obtain a yield. They are intended to show the progress of the reduction.

It will be noticed in the above runs with powdered anthracite coal that the reductions are extremely low. It was, therefore, thought advisable to check these runs with experiments on a very small scale in porcelain crucibles, in such a manner that there could be no doubt as to the time during which the charge was maintained at the temperature in question.

A number of such runs was made with a thermo-element near the center and at the outside of the charge. In the small furnace used, the crucible with its charge came to temperature in a very few minutes, so that the outside and inside thermo-element agreed to within 20° C. Approximately this condition was maintained throughout the run.

The results of the previous runs with powdered anthracite coal were confirmed by these small scale runs, and a satisfactory complete reduction could not be obtained at temperatures much below 1200° C.

#### REDUCTION OF $\text{Co}_3\text{O}_4$ WITH POWDERED CHARCOAL

Further experiments were tried on the reduction of  $\text{Co}_3\text{O}_4$  with very finely powdered charcoal. A large number of these gave fairly concordant results, which showed a greater reduction at all temperatures than the corresponding powdered anthracite coal runs.

Without giving the details of about twenty-five runs, it may be said that complete reduction was obtained with from 20 to 30 per cent excess of powdered charcoal, at 900° C. or over, in less than an hour. At 1000–1100° C., the reduction with powdered charcoal was very much more rapid than at 900° C., often completing itself in less than 10 minutes. Of course, the time required depends, to some extent, upon the size of the furnace and charge.

#### REDUCTION OF $\text{Co}_3\text{O}_4$ WITH LAMPBLACK

Experiments on the reduction of  $\text{Co}_3\text{O}_4$  with lampblack were tried with results identical with those on the reduction of  $\text{Co}_3\text{O}_4$  with powdered charcoal.

**BRIQUETS**—Experiments on the reduction of  $\text{Co}_3\text{O}_4$  with powdered charcoal were tried, forming the charge into briquets. A small percentage of molasses was used as a binder. These experiments were made under the same furnace and temperature conditions as those on the reduction of  $\text{Co}_3\text{O}_4$  with powdered charcoal in bulk. Seven such runs showed, throughout, that the reduction was not very different in its velocity from the corresponding runs with powdered charcoal, although the difference was uniformly in favor of the briquetted charges. A satisfactory reduction

The molasses would correspond to the addition of about 1 per cent carbon.

could probably not be made at temperatures below 800–850° C., even briquetting the charges, as compared with 900° C. for the charges in bulk.

The preparation of metallic cobalt by reduction in briquets or rondelles offers distinct commercial advantages in that the resulting metal is in a salable form without further melting and casting.

**THE METAL**—The metal produced by reduction of cobalt oxide with carbon is sufficiently pure for most purposes; it need not contain more than a few tenths of a per cent of carbon. The following characteristic analyses are taken at random from a large number to show the nature of the metal:

ANALYSES OF METALLIC COBALT PRODUCED BY REDUCTION OF COMMERCIAL COBALT OXIDE WITH CARBON (PERCENTAGES)

	7—12	8-15-12	10-10-12	10-11-12	6-11-13
Co	97.05	98.50	98.84	98.62	98.30
Ni	1.50	0.65	0.61	0.50	Trace
Fe	1.00	0.58	0.56	0.15	1.30
S	0.22	0.42	0.21	0.22	0.46
C	0.20	0.22	0.24	0.13	—
Ca	0.25	0.60	0.24	0.27	0.58
Mn	—	—	0.06	—	—
As	—	—	—	—	0.11
SiO <sub>2</sub>	0.12	0.13	0.14	0.11	0.12

It is obvious that the oxides taken for reduction with carbon were those directly from the smelter, which had not been treated by the method outlined above to remove the impurities. The iron, nickel, sulfur and silica content could have been reduced to mere traces by purifying the oxide before reduction in accordance with the method given. We have done this repeatedly, where a pure metal was required for experimental purposes. It is, however, of importance to note that metal with very low carbon content may be made by direct reduction of the oxide with carbon.

#### CONCLUSIONS

I. Reduction of  $\text{Co}_3\text{O}_4$  with powdered anthracite coal does not take place rapidly enough to make it commercially interesting, either in the oil-fired crucible type of furnace or in the electric crucible type of furnace, until a temperature in the neighborhood of 1200° C. is reached.

II. In either the oil-fired crucible type of furnace or in the electric crucible type of furnace, substantially complete yields of metallic cobalt may be obtained by reduction of  $\text{Co}_3\text{O}_4$  with powdered anthracite coal, in the neighborhood of 1200° C., for not more than 1 hour, with subsequent rapid melting and pouring.

III. With the oil-fired crucible furnace, using unlined graphite crucibles, complete yields are obtained with powdered anthracite coal only when there is an excess of approximately 10 per cent of this latter.

IV. With the electric crucible type of furnace used by us, complete reduction may be obtained, using only the theoretical quantity of powdered anthracite coal. In this furnace there is a considerable reduction due to the carbon monoxide atmosphere caused by the carbon resistor plates.

V. Both in the oil-fired and in the electric crucible type of furnace, greater reductions of  $\text{Co}_3\text{O}_4$  are obtained using powdered charcoal than with powdered anthracite coal, at corresponding temperatures.

VI. With the oil-fired or electric crucible type of furnace, complete reduction may be obtained with powdered charcoal at 900° C. or higher. For this reduction a considerable excess of charcoal was required: under our conditions from 20 to 30 per cent.

VII. Powdered lampblack shows results in accordance with those for powdered charcoal.

VIII. Briquetting the charges with an organic binder tends to increase the rate of reduction at all temperatures. A minimum of about 800° C. may be employed for the reduction of  $\text{Co}_3\text{O}_4$  with charcoal in the form of briquets as against 900° C. for the same charge in bulk.

IX. With sufficient carbon to get a complete yield of metal, the final product need contain only about 0.2 per cent of carbon.

X. At this laboratory, in an electric furnace not especially designed for this work, we reduce enough oxide to make 56 pounds of the metal in an eight-hour day, with the furnace absorbing 12 kw. Thus, on a commercial basis, the power charge for this reduction would be small.

#### II—PREPARATION OF METALLIC COBALT BY REDUCTION OF THE OXIDE WITH HYDROGEN

**METHOD AND APPARATUS.**—These experiments consisted in placing an alundum boat, containing a weighed amount of dried cobalt oxide, in a horizontal tube electric resistor furnace, maintaining its temperature therein constant for a definite length of time, during which a stream of hydrogen gas was passed through the furnace. A schematic sketch of the apparatus is shown in Fig. 1.

After purification, the hydrogen entered the furnace

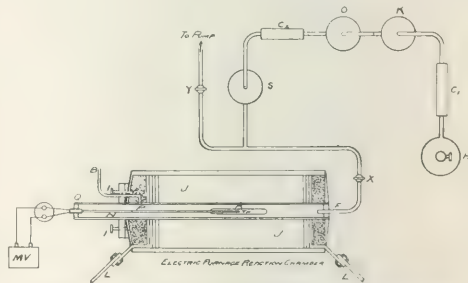


FIG. 1. ARRANGEMENT OF APPARATUS FOR REDUCTION OF  $\text{Co}_3\text{O}_4$  BY HYDROGEN

H = Hydrogen Tank O = KOH Tower Y = Stop Cock  
C<sub>1</sub> and C<sub>2</sub> = Hot Copper S = H<sub>2</sub>SO<sub>4</sub> Washer L = Leads to Ammeter  
K = K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> Tower J = Carbon Rings Z = Stop Cock and Bus Bars

at F and the excess was burned at B. During the run the exit for the gas was through the by-pass PB, the end Q being sealed.

The heating element of the furnace itself was a series of co-axial carbon ring plates, which could be pressed together more or less tightly by suitable screws. The furnace was supplied with alternating current at 25 volts from a transformer, and could be controlled at any temperature up to 1350° C.

The details of the furnace are shown in Fig. 2. The temperature measurements were made by a

platinum-rhodium thermo-element Th, and readings were taken at frequent intervals on a very sensitive millivoltmeter. In this way, the temperature was maintained substantially constant by hand regulation of the screws I. All temperature measurements were made with thermo-elements calibrated at frequent intervals, in the usual way, against known melting points.

**CONDUCTING A RUN**—After having heated the furnace to the desired temperature, by a suitable current through the carbon rings, runs were made as follows:

(a) After closing the cock X, which separates the purifying system from the furnace, the air was exhausted from the purifying system by opening cock Y, and operating a pump.

(b) Gas burners were lighted to heat copper filings in tubes C<sub>1</sub> and C<sub>2</sub>.

(c) Solutions of potassium bichromate, potassium hydrate and sulfuric acid were started flowing through the purifying towers K, O and S, which were partially filled with glass beads.

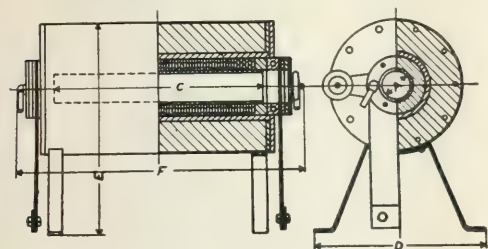


FIG. 2.—DETAILS OF ELECTRIC FURNACE FOR REDUCTION OF  $\text{Co}_2\text{O}_3$  WITH HYDROGEN

(d) Cock Y was closed and cock at outlet of hydrogen tank H was partially opened to allow a flow of hydrogen into the purifying system, until the pressure inside the system was a little greater than atmospheric pressure.

(e) Cock X was now opened to allow hydrogen to flow into the hot furnace.

(f) Flow of hydrogen was adjusted by cock at outlet of hydrogen tank H, until hydrogen burned freely at outlet end of furnace B. During the run the end Q was closed, and the gas escaped through the by-pass P-B.

(g) When adjustment (f) was satisfactory, assuring an excess of hydrogen within the furnace, the weighed dried alundum boat, containing the charge of cobalt oxide, was placed in the hot furnace at the position A, and the time noted.

(h) The run proper had now begun, during which observations of time, temperature, and power were made, and the furnace adjusted to keep the temperature constant.

(i) After a definite time, the boat, with its contents, was withdrawn from the centre of the furnace to the overhanging cool end of the furnace core N, in which it was allowed to cool, but through which, during the cooling, hydrogen was passed.

(j) When cool, the boat was removed to a desiccator and weighed.

## II—COBALT OXIDE REDUCTION WITH HYDROGEN—COOLING IN AN ATMOSPHERE OF HYDROGEN

The cobalt oxide used for the following runs, I to IX, analyzed as follows in percentages:

Co	72.3	Ca	0.15
Ni	Trace	S	0.052
Fe	0.10	Sub.	0.39

It will be noticed that this oxide contained 72.4

TABLE III. REDUCTION OF COBALT OXIDE WITH HYDROGEN

		Temperature ° C.		Time of reduction Minutes	Loss in weight Per cent	Reduction 100 = complete
Run	Boat	Mean	Average deviation			
I	I	585	1.3	5	25.5	94.2
				15	25.4	94.0
				5	25.8	95.6
II (a)	I	584	1.0	15	26.0	96.2
				30	26.6	98.3
				60	26.2	97.0
				15	26.1	96.8
				30	26.2	97.0
				60	26.1	96.8
III	II	609	4.2	7	16.8	62.2
				15	22.1	81.8
				30	22.4	83.0
				60	25.2	93.0
IV	I	597	2.0	7	25.3	94.0
				15	25.4	94.2
				30	25.4	94.2
				7	25.4	94.2
V	IV (c)	598	1.7	15	25.5	94.3
				60	25.5	94.3
				60	25.8	95.7
				120	25.7	95.3
VI	I	727	1.5	5	26.5	98.1
				10	26.5	98.1
				30	26.6	98.5
				60	26.6	98.5
				5	26.6	98.5
				10	26.5	98.1
VII (c)	I	824	4.3	30	26.6	98.5
				5	26.6	98.5
				15	26.7	98.9
				30	26.75	98.8
				60	26.75	98.8
				150	26.8	99.0
VIII	II	965	1.0	2.5	26.61	98.4
				5	26.71	98.7
				15	26.75	98.8
				30	26.75	98.8
				60	26.80	99.0
				1	25.6	94.8
IX	I	1073	2.1	5	26.9	99.7
				30	27.1	100.0
				60	27.1	100.0
				1	26.8	99.1
				5	26.9	99.4
				30	26.9	99.4
IX	II	1073	2.1	60	27.0	99.7
				2	26.28	96.8
				5	26.90	99.4
				30	27.00	99.7
				60	27.05	99.9
				1	24.38	90.0
IX	II	1073	2.1	5	26.90	99.7
				30	27.00	99.7
				60	27.10	100.0
				2	26.28	96.8

(a) It was noted at the close of this run that there was a slight oxidation at one point in the boat.

(b) All the reduced samples were steel-gray.

(c) Boat showed slight reoxidation at one end when removed from furnace.

(d) This final material analyzed 97.25 and 97.30 per cent cobalt on duplicates. The material resulting from this run contained 0.75 per cent of unreduced  $\text{CaSO}_4$ ,  $\text{CaO}$  and  $\text{SiO}_2$ , and 1.4 per cent of oxygen presumably in the form of  $\text{Co}_2\text{O}_3$  (the stable oxide at 598° C., see following article, page 115), and 0.10 per cent of nickel and iron. It should, therefore, contain  $100 - 2.3 = 97.7$  per cent of cobalt. This checks with the value determined by analyses, 97.3, to within the accumulative error in the analyses.

(e) The product from this run seemed to be of a slightly lighter gray shade than that from the runs at lower temperatures.



per cent of the metals cobalt, nickel and iron, in the form of oxides which may be computed without error to be cobalt oxide. Any sample contains, therefore, 0.75 per cent of unreducible calcium sulfate, calcium oxide and silica, 99.2 per cent of cobalt oxide running  $72.4/99.2 = 72.9$  per cent in cobalt. This oxide, therefore, corresponds very closely to  $\text{Co}_3\text{O}_4$ . The oxygen content of the substance which could be reduced by hydrogen, is equal to 27.1 per cent of 99.2 per cent = 27.0 per cent. This figure is accurate to within the experimental error of the runs, and is used as the basis of the following computations; that is to say, in the column headed "Percentage loss in weight," 27 per cent would represent complete reduction, and the last column headed "Reduction where 100 per cent is complete reduction" is computed in terms of 27 per cent actual reduction as total. The boats used ranged in weight from 5 to 6.5 grams and the charges of cobalt oxide from 2.0 to 2.1 grams.

The check between the composition of the oxide used for these hydrogen reduction experiments, as determined by analysis and as determined by the reduction experiments, is entirely satisfactory (see following article, p. 115).

A number of the early experiments to reduce  $\text{Co}_3\text{O}_4$  with hydrogen were made allowing the reduced product to cool in the atmosphere. In every case reoxidation took place. These runs were made at various temperatures from  $500^\circ\text{C}$ . to  $1000^\circ\text{C}$ ., and curiously enough the reoxidation at the higher temperatures was progressively less than at the lower temperatures.

#### CONCLUSIONS

I. The reduction of  $\text{Co}_3\text{O}_4$  to metallic cobalt by hydrogen gas takes place very rapidly at all temperatures above  $500^\circ\text{C}$ .

II. At temperatures between  $500^\circ\text{C}$ . and  $700^\circ\text{C}$ ., over 90 per cent of the reduction of  $\text{Co}_3\text{O}_4$  to Co takes place in a few minutes, but a further reduction takes place very slowly, if at all.

III. Between  $700^\circ\text{C}$ . and  $1100^\circ\text{C}$ ., the amount of reduction of  $\text{Co}_3\text{O}_4$  to Co which takes place during the first few minutes increases very rapidly with rising temperature, and at the higher temperatures it is complete.

IV. The hydrogen reduction method is to be especially recommended for the production of moderate quantities of very pure carbon-free cobalt for special purposes, just as it has been used for the production of metallic tungsten.

V. For the production of cobalt from  $\text{Co}_3\text{O}_4$  by hydrogen, the charge must be completely cooled in an atmosphere of hydrogen.

#### III. PREPARATION OF METALLIC COBALT BY REDUCTION OF THE OXIDE WITH CARBON MONOXIDE

**METHOD AND APPARATUS**—These experiments were performed by placing an alundum boat, containing a weighed amount of dried cobalt oxide, in a horizontal tube electric resistor furnace, maintaining its temperature therein constant for a definite length of time, during which a stream of carbon monoxide was passed through the furnace (see Figs. 3 and 4).

**CARBON MONOXIDE GENERATOR**—The carbon mon-

oxide was supplied by passing carbon dioxide over hot wood charcoal, which reduced it according to the reaction,  $\text{CO}_2 + \text{C} = 2\text{CO}$ .

Carbon dioxide, after purification, entered the lower end of the carbon monoxide generating furnace at G.

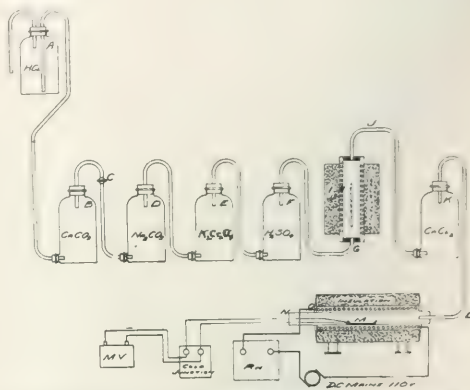


FIG. 3. APPARATUS FOR REDUCTION OF  $\text{Co}_3\text{O}_4$  WITH CARBON MONOXIDE

This furnace was of the electric resistance type, made by winding nichrome wire over an alundum cylinder, the two being embedded in magnesite cement, and insulated within a cylindrical iron container. The wire is shown in section at H and the iron container at I. The entire core of the furnace was filled with wood charcoal, maintained at about  $1000^\circ\text{C}$ . by an appropriate current through the heating element. As a result, carbon monoxide gas left the generator at J, with a certain amount of moisture which was absorbed by passing through calcium chloride at K. Thus, substantially pure carbon monoxide entered the reaction furnace proper at L, passed over the alundum boat M, with its cobalt content, and the excess burned off at N.

**THE REACTION FURNACE**—The reaction furnace proper is shown in Fig. 3. It consisted of a central silica tube LN, 2 ft. in length, and 1 in. in internal

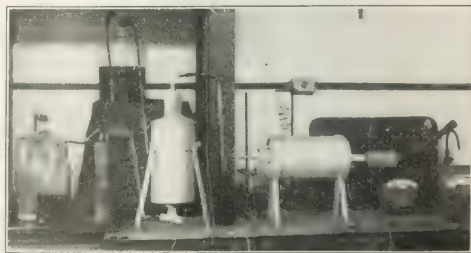


FIG. 4

diameter. This was wound with calorite or nichrome wire, of such resistance that it could be controlled by a suitable rheostat Rh on 110 volt direct current mains, to maintain a temperature constant to within less than  $10^\circ$  during a run, at any temperature up to  $1000^\circ\text{C}$ .

**TEMPERATURE MEASUREMENTS**—The temperature measurements were made by a platinum platinum-rhodium thermo-element Th, and readings were taken at frequent intervals on a very sensitive millivolt-meter Mv. The thermo-elements used for the temperature measurements were calibrated at frequent intervals.

**COOLING CHARGE IN CARBON MONOXIDE ATMOSPHERE**—The silica tube NL extended beyond the end of the furnace proper from O to N. The portion O-N was 1 ft. in length and was kept cool by a circulation of water, so that at the close of a run the boat was removed from the centre of the furnace to O-N, where it cooled to room temperature in the stream of CO gas.

**CONDUCTING A RUN**—After having heated the reaction furnace, and the CO producer furnace, by suitable currents, to the desired temperature, runs were made as follows:

(a) The cock C was opened to allow CO<sub>2</sub> gas to pass through the purifying system DEF into the producer furnace at G.

(b) The CO gas generated in the producer furnace GJ passed through the reaction furnace LN and was lighted at N.

(c) The weighed dried boat with its charge was introduced into the exterior ON of the reaction furnace.

(d) Temperature and time observations were begun, and when the desired temperature had been reached, the boat was moved to M.

(e) The run proper had now begun, during which observations of time and temperature were made and the rheostat Rh adjusted to keep the temperature constant.

(f) After a definite time the boat, with its contents, was withdrawn from M to ON, where it was allowed to cool in a current of carbon monoxide gas.

(g) When the boat was cool, the current of carbon monoxide was gradually diminished by closing the cock C, until it was finally entirely cut off.

(h) When the boat was cooled to room temperature, it was removed to a desiccator and weighed.

#### COBALT OXIDE FOR CARBON MONOXIDE REDUCTION EXPERIMENTS

The cobalt oxide for the CO reduction experiments was identical with that used for the hydrogen reduction experiments so that the column headed "Reduction where 100 per cent is complete reduction" is computed in terms of 27.0 per cent actual reduction as total.

A number of the first runs were made, reducing Co<sub>3</sub>O<sub>4</sub> with CO and allowing the reduced product to cool in the atmosphere before weighing. Under these conditions, reoxidation took place rapidly, so that but a single pair of typical runs are given. The boats used weighed 10.5+ and 13.3 grams and the charges of cobalt oxide, 2—grams.

The reoxidation of cobalt oxide after reduction

with carbon monoxide takes place with great vigor. If the boat be withdrawn from the hot furnace directly into the atmosphere, it may be seen to glow with great brilliancy. If the content of the boat, while still warm, be snapped out on the floor, it will reoxidize with such vigor that a cracking sound, as of a mild explosion, attends the reaction, i. e., the reoxidation taking place according to the reaction  $6\text{CoO} + \text{O}_2 = 2\text{Co}_3\text{O}_4$  is extremely exothermic.

In the runs of Table IV, during the first part of the run, and up to the time that it began to gain in weight,

TABLE IV—REDUCTION OF Co<sub>3</sub>O<sub>4</sub> WITH CO COOLING IN AIR

Number	Run	Boat	Temperature		Time of reduction Minutes	Per cent loss in weight	Reduction 100 = complete
			Mean	Average deviation			
I	I		602°	9	15	10.6	39.3
					30	11.1	41.1
					45	10.8	39.9
					60	12.9	47.8
					75	12.9	47.8
					82	11.8	43.6
					92	11.3	41.8
					107	7.8	39.6
II	II		594	12	30	12.4	46.0
					45	11.7	43.3
					75	13.2	48.8
					97	12.3	45.5
					112	11.9	44.0
					142	10.3	38.2

the Co<sub>3</sub>O<sub>4</sub> in both boats gradually became a gray color. This gray material is CoO. At the end of the run it was black again.

On account of the irregularities of reoxidation, the furnace reaction chamber was lengthened by substituting a silica tube of length LN for the one of length LO as shown in Fig. 3. The overhanging tube ON, about 1 ft. in length, was cooled by water, and served as a cooling chamber for the boat while CO gas was still passed through it.

The following runs, representative of a large number, show the rate of the reduction of cobalt oxide by CO gas when the cooling was controlled so that no reoxidation could take place. The boats used weighed about 8 grams and the charges of oxide about 2 grams.

In Run III, Table V, the oxide became a greenish gray color at the end of the first five minutes, and a uniform steel-gray color at the end of fifteen minutes. From then on it began to gain in weight, due to a deposit of carbon. At the close of many runs at this temperature, there was an extremely heavy deposit of carbon in the boat.

This run was typical of a number, which showed a reduction from the original black oxide to the green, followed by a change from the green to the gray, and then a gain in weight, due to a deposit of carbon. The only possible source of carbon was from the carbon monoxide gas, so that the finely divided metallic cobalt, which was formed during the first stage of the reduction of the gray oxide, probably acted catalytically to decompose carbon monoxide gas at this temperature. This is an extremely interesting decomposition which might well be studied with considerable care.

TABLE V. REDUCTION OF COBALT OXIDE BY CARBON MONOXIDE GAS  
CONTAINING IN CO GAS

Run	Boat	Temperature °C.		Time of reduction Minutes	Loss in weight Per cent	Reduction 100 = complete
		Mean	Average deviation			
III		31.	3	5	18.2	67.3
				15	25.2	93.2
				45		
				60	Deposit of carbon	
IV	I	451	3	5	22.1	81.8
				15	13.4	49.5
				45	21.4	79.2
V	I	453	3	15	13.2	48.4
				45	Gain	
				60	Gain	
				5	16.2	60.0
VI	I	583	5	15	26.4	97.8
				35	26.8	98.0
				50	26.9	99.6
				65	27.0	100.0
VII	II	596	3	20	26.5	98.1
				30	26.6	98.4
VIII	I	600	5	10	21.0	77.9
				5	21.2	78.3
IX	II	597	6	15	24.7	91.0
				49	26.3	97.7
				69	26.7	98.8
				86	27.2	100.0
X		611	6	146	27.1	100.0
				5	25.7	95.0
				15	26.3	97.2
				45	26.7	99.0
XI	I	594	6	60	26.7	99.0
				5	25.6	94.9
				15	26.5	98.0
				45	26.5	98.0
XII	II	601	1	60	26.6	98.4
				5	26.7	99.0
				15	26.8	99.3
				45	26.9	99.8
XIII		754	3	60	26.9	99.8
				5	26.8	99.6
				15	26.8	99.6
				45	26.9	99.8
XIV		752	4	60	26.9	99.8
				5	24.9	92.3
				15	26.7	99.1
				45	26.8	99.6
XV		749	3	60	26.8	99.6
				150	26.8	99.6
				5	26.0	96.2
				15	26.6	98.8
XVI		751	3	45	26.7	99.1
				60	26.7	99.1
				5	26.5	98.3
				15	26.9	99.8
XVII		900	4	45	27.0	100.0
				60	27.0	100.0
				5	26.6	98.8
				15	26.8	99.7
XVIII		900	4	45	26.9	99.8
				60	26.9	99.8

A strong odor of hydrocyanic acid was noticed throughout run IV. After five minutes or so, a deposit of carbon began to form in the boat, due to the decomposition of carbon monoxide by finely divided cobalt, as in the runs at 350° C.

Throughout run V a strong odor of HCN was noticed. This is true of all the reductions of cobalt oxide with carbon monoxide in the neighborhood of 450° C.

These two runs are typical of a large number of similar ones. Our observations seem to show that the decomposition of CO by cobalt takes place only through a temperature interval in the neighborhood of from 300–450° C.

The check between composition of the oxide used for

these CO reduction experiments, as determined by analysis and as determined by the reduction experiments themselves, is entirely satisfactory. (See following article, p. 115.)

#### CONCLUSIONS

I. The reduction of  $\text{Co}_3\text{O}_4$  to metallic cobalt by carbon monoxide gas takes place very rapidly at all temperatures above 600° C.

II. Between 350° C. and 450° C., carbon monoxide at first reduces  $\text{Co}_3\text{O}_4$  to cobalt, but after a time the finely divided cobalt decomposes the CO gas, depositing carbon.

III. At temperatures between 500° C. and 750° C., over 90 per cent of the reduction of  $\text{Co}_3\text{O}_4$  to Co takes place in a few minutes, but a further reduction to completion takes place very slowly.

IV. Between 750° C. and 900° C., the amount of reduction of  $\text{Co}_3\text{O}_4$  to Co, which takes place during the first few minutes increases very rapidly, and at the higher temperatures it is complete.

V. Where producer gas is available it should offer a cheap and efficient means of producing large quantities of pure metallic cobalt from the oxide.

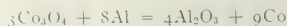
VI. For the production of cobalt from  $\text{Co}_3\text{O}_4$  by CO, the charge must be completely cooled in an atmosphere of CO.

#### IV—REDUCTION OF COBALT OXIDE WITH ALUMINUM

The heat of formation of a molecular weight in kilograms of aluminum oxide ( $\text{Al}_2\text{O}_3$ ) is 392,600 kilogram-calories, and is greater than that of any other metallic oxide. The molecular heat of formation of ferric oxide ( $\text{Fe}_2\text{O}_3$ ) is correspondingly 195,600 kilogram-calories. It is therefore obvious that if finely divided aluminum be intimately mixed with ferric oxide ( $\text{Fe}_2\text{O}_3$ ), the latter, possibly in the form of rolling mill scale, that the reaction  $\text{Fe}_2\text{O}_3 + 2\text{Al} = \text{Al}_2\text{O}_3 + 2\text{Fe}$  will take place, provided the temperature be raised at some point in the mixture sufficient to start the reaction. This principle has been used by the Goldschmidt Thermit Co. to produce molten iron for welding purposes.

It is obvious that for every 160 kilograms of ferric oxide and 54 kilograms of metallic aluminum that are mixed together and fired in this way, there are developed 392,600 — 195,600 = 197,000 kilogram-calories of heat. This is sufficient to raise the entire mass to a white heat, so that the molten iron readily settles to the bottom from where it may be tapped.

In a similar manner, metallic cobalt may be prepared by reduction of cobalt oxide with aluminum according to the reaction:



The molecular heat of formation of  $\text{Co}_3\text{O}_4$  is 193,400 calories.<sup>1</sup>

It is therefore obvious that for every 723 kilograms  $\text{Co}_3\text{O}_4$  and 216 kilograms of aluminum that are mixed together and fired, there are developed  $4 \times 392,600 - 3 \times 193,400 = 990,200$  kilogram-calories of heat. We would, therefore, expect a reaction

<sup>1</sup> *Table: Annales Internationales des Constantes*, 1, 428 (1910).



quite as vigorous, if not more vigorous, than the corresponding one with ferric oxide.

Experiments were tried, October, 1912, using a standard Goldschmidt Thermit conical welding furnace. Into this was charged 5-10 lbs. of finely divided  $\text{Co}_3\text{O}_4$  with the theoretical amount of aluminum, according to the equation  $3\text{Co}_3\text{O}_4 + 8\text{Al} = 4\text{Al}_2\text{O}_3 + 9\text{Co}$ . The reaction was started by lighting a fuse of finely divided aluminum and potassium chlorate, rolled in a piece of tissue paper. The furnace fired with extreme violence, in every case becoming an intense white heat. The vigor of the reaction was so great that the lining of the furnace, although the best alundum-magnesite-cement mixture, would stand up for only two or three charges.

**THE METAL**—The metal produced in this manner was readily tapped from the bottom of the furnace into iron or sand moulds. It frequently contained less than 0.1 per cent of aluminum, and, of course, was carbon-free.

The various metals, chromium, molybdenum, etc., made by the Goldschmidt Co. by this method, as they have come to us, run about 0.5 per cent in aluminum and are carbon-free.

#### CONCLUSIONS

This aluminum reduction method can obviously be used with considerable satisfaction where absolutely carbon-free metal is required, and where a somewhat increased cost is not prohibitive. Moreover, it affords a method of preparing cobalt-aluminum alloys at once by adding an excess of metallic aluminum.

The price of crude aluminum, such as might be used for this purpose, is in the neighborhood of 17 cts. per lb. One pound of aluminum will reduce and melt in this way a little over two pounds of metallic cobalt. Therefore, there is a charge of 17 cts. in the form of 1 lb. of metallic aluminum, for the power for reducing and melting two pounds of metallic cobalt. There might, of course, be some return for the fused aluminum oxide which resulted from the process, but even allowing liberally for this, the costs are high as compared with the carbon and carbon monoxide methods of reduction described elsewhere in this paper.

It is obvious that the heating costs must be high by the aluminum method, for heat is being supplied at a temperature greater than  $2100^\circ\text{C}$ ., that is, at a temperature far in excess of what is required for the reduction of the oxide and the melting of the metal, and with consequent attendant increased losses, due to conduction and radiation.

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#### OXIDES OF COBALT<sup>1</sup>

By HERBERT T. KALMUS

The following oxides of cobalt have been described in various places throughout the literature:  $\text{Co}_2\text{O}$ ,  $\text{CoO}$ ,  $\text{Co}_8\text{O}_9$ ,  $\text{Co}_6\text{O}_7$ ,  $\text{Co}_4\text{O}_5$ ,  $\text{Co}_3\text{O}_4$ ,  $\text{Co}_7\text{O}_{10}$ ,  $\text{Co}_2\text{O}_3$ ,

$\text{Co}_{12}\text{O}_{19}$ ,  $\text{Co}_3\text{O}_5$ ,  $\text{CoO}_2$ , and considerable disagreement is to be found among the statements concerning them.

The existence of many of these compounds is doubtful, and there are but three of them which particularly concern the commercial manufacturer of cobalt oxide:  $\text{Co}_3\text{O}_4$ ,  $\text{Co}_6\text{O}_7$ , and  $\text{CoO}$ . These concern us in the production of metallic cobalt. We shall, therefore, describe these three oxides as we have observed them in the course of the experiments reported in our previous article, p. 107 of this issue of *THIS JOURNAL*.

#### COBALTO-COBALTIC OXIDE, $\text{Co}_3\text{O}_4$

The ordinary black commercial cobalt oxide which has been prepared from the hydrate, by calcining in the neighborhood of  $750^\circ\text{C}$ ., is a mixture of  $\text{Co}_3\text{O}_4$  and  $\text{Co}_6\text{O}_7$ , but largely the former.

There is an abundance of proof throughout the previous paper that this black oxide is largely  $\text{Co}_3\text{O}_4$ , of which the following may be particularly noted:

(a) The purified cobalt oxide used for hydrogen reduction experiments, making allowance for the impurities according to the analyses, was computed to contain 72.9 per cent cobalt. The hydrogen reduction experiments, using this same oxide, showed, wherever the reduction was complete, a loss of oxygen amounting to 27.0 per cent. As was shown on p. 111, this checks with the 72.9 per cent of cobalt, with allowance made for the slight impurities. Hence, this black oxide must be largely  $\text{Co}_3\text{O}_4$ , as may be seen from the following theoretical percentages:

	Per cent cobalt
$\text{Co}_3\text{O}_4$ .....	71.1
$\text{Co}_6\text{O}_7$ .....	73.4
$\text{Co}_4\text{O}_5$ .....	75.9
$\text{CoO}$ .....	78.8

(b) The purified cobalt oxide used for the carbon monoxide experiments, making allowance for the impurities according to the analysis, was computed to contain 72.9 per cent cobalt. The CO reduction experiments, using this same oxide, wherever reduction was complete, showed a loss of oxygen amounting to 27.0 per cent. As was shown on pp. 110 and 111, this checks with 72.9 per cent cobalt, with allowance made for the slight impurities. Hence, this black oxide must be largely  $\text{Co}_3\text{O}_4$  according to the table under (a).

(c) As a further proof that the black oxide calcined at a good red heat is  $\text{Co}_3\text{O}_4$ , the following experiment was tried:

A pure black hydrate of cobalt was made from electrolytic cobalt by the potassium-cobalti-nitrite method. This was calcined to constant weight at  $105^\circ\text{C}$ ., yielding a chocolate-brown powder, which was uniform under the microscope. Several samples of this brown powder were calcined to constant weight at  $640^\circ\text{C}$ ., and in each instance showed a loss of water between 11.5 per cent and 11.8 per cent. Therefore, the brown powder corresponds very closely to  $\text{Co}_2\text{O}_3 \cdot \text{H}_2\text{O}$ .

The material resulting from these calcinations was a black powder identical in appearance under the microscope with the black cobalt oxide of commerce.

<sup>1</sup> Published by permission of the Director of Mines, Ottawa, Canada.  
See footnote to previous article, page 107.

A sample of this previously calcined black oxide was calcined at a red heat to a constant weight of 0.8300 gram. The same sample was then completely reduced with a mixture of hydrogen and carbon monoxide gas at 900° C., which brought it to a constant weight of 0.6063 gram. Thus, the loss in weight was 27.2 per cent. Except for traces, this material was free from non-reducible substances, so that the oxide contained 72.8 per cent cobalt, against 73.4 per cent corresponding theoretically with  $\text{Co}_3\text{O}_4$ . This was checked several times, which substantiates the statement that black cobalt oxide is  $\text{Co}_3\text{O}_4$ .

(d) A further experiment was as follows: Black oxide was brought to constant weight at 640° C., and immediately thereafter brought to constant weight by heating to 1020° C. This experiment was tried several times and in every instance the percentage loss in weight was found to be very close to 7.1 per cent. The resulting gray oxide at 1020° C. analyzed 79.3 per cent Co, corresponding very well with CoO (78.8 per cent Co).

The theoretical loss in passing from  $\text{Co}_3\text{O}_4$  to CoO is 6.6 per cent. As against this, the theoretical loss passing from  $\text{Co}_3\text{O}_4$  to  $\text{Co}_6\text{O}_7$  would be 3.3 per cent, and correspondingly, passing from  $\text{Co}_6\text{O}_7$  to CoO the loss would be 3.3 per cent. Thus, there is very little doubt but that our reduction of the black oxide formed at red heat, to the gray at 1020° C., corresponds with the transition from  $\text{Co}_3\text{O}_4$  to CoO.

(e) Two independent samples of brown  $\text{Co}_2\text{O}_3 \cdot \text{H}_2\text{O}$ , calcined to constant weight at 640° C., analyzed for cobalt,<sup>1</sup> respectively, 74.7 per cent and 73.8 per cent. This analysis is between  $\text{Co}_3\text{O}_4 = 73.4$  per cent Co and  $\text{Co}_6\text{O}_7 = 75.9$  per cent Co. This black oxide is therefore largely  $\text{Co}_3\text{O}_4$  with some  $\text{Co}_6\text{O}_7$ .

The black hydrated cobalt oxide, as formed commercially by precipitation of a chloride or sulfate solution with bleach,<sup>2</sup> or the brown  $\text{Co}_2\text{O}_3 \cdot \text{H}_2\text{O}$ , may be calcined at any temperature between 385° C. and 910° C., to yield substantially the same product, but in practice it is better to calcine at a good red temperature, in order that the calcination may take place with reasonable speed.

That there is a range between 385° C. and 910° C., through which very little oxidation or reduction of the black  $\text{Co}_3\text{O}_4$  takes place, is shown by the following figures:

Starting with  $\text{Co}_3\text{O}_4$ , heated to constant weight at 385° C. the loss in weight heating it to constant weight is

at 640° C. . . . .	0.7 per cent	at 860° C. . . . .	2.4 per cent
at 770° C. . . . .	1.2 per cent	at 910° C. . . . .	2.5 per cent

Just above 910° C., however, the reduction begins to take place very rapidly, and the black  $\text{Co}_3\text{O}_4$  reacts to become gray CoO. Continuing the experiment for which the figures above are given, we have loss in weight heating it to constant weight

at 980° C. . . . . 5.0 per cent

This oxide,  $\text{Co}_3\text{O}_4$ , shows no trace of being magnetic.

<sup>1</sup> Including very small amounts of Ni and Fe.  
<sup>2</sup> See page 107.

## THE OXIDE $\text{Co}_6\text{O}_7$

$\text{Co}_6\text{O}_7$  is not to be distinguished from  $\text{Co}_3\text{O}_4$  either in appearance or in method of preparation; in fact, we have not succeeded in forming a pure oxide of cobalt which analyzed very close to 75.9 per cent. On the other hand, as will be noticed in many places throughout this paper, the analyses of the material obtained by calcining at a red heat are frequently something in excess of 73.4 per cent after making allowance for impurities. We, therefore, assume that a certain amount of  $\text{Co}_6\text{O}_7$  accompanies the  $\text{Co}_3\text{O}_4$ .

## COBALT MONOXIDE, CoO

Cobalt monoxide is the stable oxide of cobalt when calcination takes place at a high temperature, that is, in the neighborhood of 1000° C. It is a gray powder and reacts to form the metal by heating with carbon monoxide gas at any temperature above 450° C., or with hydrogen gas at any temperature above 250° C.

Cobalt monoxide also exists in an allotropic form which is a yellow-green powder. Either the yellow-green or the gray cobalt monoxide oxidizes to  $\text{Co}_3\text{O}_4$ , or to a mixture of  $\text{Co}_3\text{O}_4$  and  $\text{Co}_6\text{O}_7$ , when heated in the air to any temperature between 385° C. and 910° C. The yellow-green variety is readily formed by heating  $\text{Co}_3\text{O}_4$  with 2 to 3% by weight of C at temperatures in the neighborhood of 900° C.

Numerous analyses of the purified gray oxide have been made, which range around the theoretical value 78.8 per cent. The following experiment was tried to prove that yellow-green oxide is an allotropic form of the gray CoO: Black  $\text{Co}_3\text{O}_4$  calcined at 640° C. to constant weight was then calcined to constant weight at 1020° C. It lost, thereby, 7.1 per cent in weight, and the product was gray CoO. Yellow-green CoO, produced by the reduction of black  $\text{Co}_3\text{O}_4$  with hydrogen at 300° C., was calcined to constant weight in air at 640° C., gaining, thereby, 6.5 per cent in weight and becoming black. This experiment, like the others, indicates that the gray and the yellow-green oxides are identical to within such limits that if the yellow-green be CoO, the gray cannot depart from it by more than the formula  $\text{Co}_3\text{O}_4\text{O}_{20}$ . Such differences as there are, however, seem to show uniformly that the gray has slightly the greater oxygen content of the two.

A further experiment was performed with the yellow-green oxide as follows: Freshly prepared yellow-green oxide was reduced to metal with hydrogen and carbon monoxide gas, and brought to constant weight. During the reduction, the loss in weight was 21.5 per cent in one case and 21.3 per cent in another, corresponding very well with the reduction of CoO to metallic cobalt which would be 21.3 per cent.

Both the gray and the green CoO are nonmagnetic, and the samples of gray prepared by us, as well as those obtained from commercial sources, are homogeneous powders under 100 diameters magnification.

# THE ANALYTICAL CONSTANTS OF HYDROGENATED OILS

By CARLETON ELLIS

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The hydrogenation of oils has to such an extent changed certain of the constants by which oils and fats are at least in part identified, namely, the iodine number and the specific gravity, that the identification of a fat or fatty mixtures, often heretofore a troublesome matter at best, now promises to become even more difficult.

The reduction of the iodine number through the introduction of hydrogen into the oil, in a sense is arbitrary; there is no difficulty in reducing the iodine number almost to zero through the hydrogenation process, or at any moment to interrupt the operation and from one and the same initial material to produce products having the most varied iodine numbers.

The specific gravity and melting point advance hand in hand as saturation progresses, the specific gravity approaching that of tristearine, while the resultant melting point in considerable measure depends upon the molecular weight and the hydroxyl content of the fatty acid components of the oil. The specific gravity of a hardened cottonseed oil whose iodine number had been reduced to zero was found by Normann and Hugel<sup>1</sup> to be 0.9999 at 15° C., while they note that tristearine has a specific gravity of 1.0101 at the same temperature.<sup>2</sup>

The index of refraction also is strongly modified. A sample of fish oil at 56° C., according to Normann and Hugel, showed a figure of 53.8; while after hardening to an iodine number of 22.5 the index was 36° C. at the same temperature. (Scale of the Zeiss butter refractometer.)

Observations made in the writer's laboratory on the index of refraction of a number of hydrogenated oils gave the results noted below:

INDEX OF REFRACTION AT 55° C.  
(Abbe Refractometer)<sup>3</sup>

	Original Oil	Hydrogenated Oil
Corn .. . . .	1.4615	1.4514 (M. P. 55.7° C.)
Whale (No. 1) .. . . .	1.4603	1.4550 (M. P. 41.5° C.)
Soya bean .. . . .	1.4617	1.4538 (M. P. 50.3° C.)
Cocoonut oil ("olein") .. . . .	1.4429	1.4425 (M. P. 24.7° C.)
Linseed .. . . .	1.4730	1.4610 (M. P. 42.3° C.)
Palm .. . . .	1.4523	1.4517 (M. P. 38.7° C.)
Palm .. . . .	1.4523	1.4494 (M. P. 44.8° C.)
Peanut (edible) .. . . .	1.4567	1.4547 (M. P. 34.7° C.)

The gradual reduction of the index of refraction by progressive hydrogenation is shown in the following table compiled from determinations made in the writer's laboratory.

Cottonseed oil was hydrogenated for a period of ten hours and samples were drawn at one hour intervals.

<sup>1</sup> Chem. Ztg., 1913, 815.

<sup>2</sup> The specific gravity of tristearine is given by the "Chemiker Kalender" as 1.0101 at 15° C., while Lewkowitsch reports the specific gravity of a specimen of not quite pure stearine in the melted state as 0.9235 at 65.5° C.

<sup>3</sup> Refraction values are given in terms of true refractive index and also according to the arbitrary scale of the butyro-refractometer, in order to follow the data available, as rendered.

It is of interest to note that while the addition of hydrogen to fatty oils reduces the index of refraction, the addition of oxygen increases the index as is shown in the case of blown or ozonized oils.

Original Oil	Melting point	Index of refraction 55° C.
1 hour .. . . .	28.2° C.	1.4588
2 hours .. . . .	31.3	1.4577
3 " .. . . .	34.3	1.4568
4 " .. . . .	37.9	1.4557
5 " .. . . .	40.8	1.4549
6 " .. . . .	43.8	1.4540
7 " .. . . .	45.6	1.4527
8 " .. . . .	47.3	1.4518
10 " .. . . .	55.9	1.4510
		1.4496

The saponification number practically does not change. The content of free fatty acids changes but little. A sample of cottonseed oil containing 1.8 per cent fatty acid was found, after hardening to various degrees, to have a fatty acid content ranging from 1.4 per cent to 1.9 per cent. With sesame oil containing 2.44 per cent fatty acid the resulting hardened oil contained 2.55 per cent of acid. The content of unsaponifiable bodies does not essentially change. Cottonseed oil having 0.55 per cent unsaponifiable matter, after hardening, showed a content of unsaponifiable bodies ranging from 0.45 per cent to 0.55 per cent; sesame oil with an unsaponifiable content of 0.70 per cent, after hardening contained 0.85 per cent unsaponifiable.

Cholesterol and phytosterol, according to Bomer, are not changed by treating oils with hydrogen, although this is somewhat contrary to the statement of Windaus,<sup>1</sup> according to whom cholesterol may be easily reduced by the catalytic process. Willstätter and Mayer<sup>2</sup> hydrogenated cholesterol in ether solution with a platinum catalyzer.

In the case of the acetyl number more noticeable changes take place according to Normann and Hugel. When hardening castor oil, for example, the hydroxyl number in one sample dropped from 156 to 102; in another sample the number fell to 131. The hydroxyl group is thus more or less broken down by the hydrogenation process, at least under some conditions of treatment.

Acid number .. . . .	3.5
Saponification number .. . . .	183.5
Iodine number .. . . .	4.8
Acetyl number .. . . .	153.5
Acetyl number of the fatty acids .. . . .	143.1
Acid number of the fatty acids .. . . .	184.5
Saponification number of the fatty acids .. . . .	187.9
Melting point of the fat .. . . .	68° C.
Melting point of the fatty acids .. . . .	70° C.
Melting point of the acetylated acids .. . . .	47° C.

The properties of hardened castor oil have been noted by Garth,<sup>3</sup> whose observations differ somewhat from those of Normann and Hugel. As is generally known, castor oil differs materially from many other common oils in such respects as its high viscosity, solubility in alcohol and difficulty of salting out its soaps by electrolytes. Hardened castor oil dissolves in alcohol only by heating and separates on cooling, but is soluble at ordinary temperature in chloroform. The constants of one sample of hardened castor oil examined by Garth are given in the above table.

<sup>1</sup> Ber. d. chem. Ges., 1912, 3051.

<sup>2</sup> Ibid., 1908, 41, 2199.

<sup>3</sup> SEIGER Z., 1912, 1300.



These results obtained by Garth would indicate that the saponification and acetyl number do not change. The iodine number has fallen greatly and the melting point is much increased. The difference between the acid number of the fatty acids and their saponification number points to the formation of lactones. As is known castor oil has the property at high temperatures of forming anhydrides, accompanied by polymerization.

The effect of hydrogenation on color tests of oils is variable. Thus the Boudouin sesame oil test is not influenced; in fact the reaction seemingly is sharper after treatment of the oil with hydrogen, while the Halphen test is not likely to give positive results even with oils which have been only slightly hardened.

The Becchi test is operative with slightly hardened cottonseed oil, but is indistinct with highly hardened oil so that this test is significant only in event of a positive coloration.

Hardened fish oil loses all its essential characteristics such as the formation of well defined bromine compounds of the higher unsaturated fatty acids. Thus there are obtained after hardening, new fatty acids corresponding to the saturated bodies, arachidic ( $C_{20}H_{40}O_2$ ) and behenic acids ( $C_{22}H_{44}O_2$ ), which in variable amounts up to a proportion of 20 per cent and more have been observed in certain hydrogenated oils. In the hardening of rape oil behenic acid is formed from the erucic acid present. Other oils or fats with a noticeable proportion of acids with more than 18 carbon atoms in the molecule apparently scarcely ever come into the trade.

As a test for hydrogenated peanut oil, Kreiss and Roth<sup>1</sup> have given a method which consists in saponifying 20 grams of the oil with 40 cc. of alcoholic potash; then adding 60 cc. of alcohol and acidifying by the addition of 50 per cent acetic acid of which approximately 15 cc. are required. One and one-half grams of lead acetate are added and the mixture allowed to stand over night. The lead salts which separate are decomposed by boiling with 5 per cent hydrochloric acid, the fatty acids are dissolved in 50 cc. of 90 per cent alcohol with slight warming and the solution is placed in water at 15° for about one-half hour. The crystals which separate are recrystallized from 25 cc., then 12½ cc. of 90 per cent alcohol and the melting point determined. The presence of at least 5 per cent arachidic acid causes the melting point of the third crystallization to be over 70° C.

Normann and Hugel<sup>2</sup> state that this test is applicable likewise to hardened fish and rape oil. They tested a number of samples of fish oil from several sources and found in each case that the melting point of the recrystallized fatty acids was at least 70°. Normann and Hugel state that it is unnecessary with hardened fish oil to allow the lead acetate to react for several hours, it sufficing simply to let the mixture stand until cooled to room temperature; this can be hastened by cooling with water. So large a proportion of fatty acids is obtained according to this procedure that the

specified amount of alcohol is not sufficient to dissolve them. It is better to use 100–150 cc. of alcohol and heat on the water-bath until solution is affected. The application of heat should not be continued for any great length of time as arachidic acid readily forms esters. The mixture is then placed in cold water, cooled to room temperature and the separated material collected and crystallized several times from alcohol used in progressively diminishing proportions. Three crystallizations suffice for only slightly hardened fats. With fats of higher consistency one must recrystallize several times more until the melting point is constant.

In one case using hardened fish oil having a melting point of 44, three recrystallizations from alcohol gave a constant melting point of only 63°, while further recrystallization using acetone caused the melting point to advance to 76°. In doubtful cases one should try several solvent mediums. If the melting point is found to be above 70° C. Normann and Hugel think it proof that either hardened fish, rape or peanut oil is present. If one is certain of the unitary character of the oil then peanut and rape oil can be distinguished from fish oil by the cholesterol test, provided the statement of Bomer in regard to the unchangeability of cholesterol and phytosterol under ordinary conditions of oil hydrogenation is confirmed.

Data on hardened oils by Davidsohn<sup>3</sup> are tabulated below:

	M P	Acid No.	Saponification		Ash
			number	Moisture	
Talgol.....	39.3	3.4	191.0	0.10	0.07
Talgol extra.....	46.8	3.5	191.3	0.13	0.05
Candellite.....	49.0	3.2	191.0	0.20	0.08
Candelite extra.....	51.9	3.9	190.8	0.15	0.04
Coryphol.....	79.3	3.3	189.9	0.18	0.05

These hardened fish oils or other hardened oils put out under the trade names indicated are manufactured by the Germania Oil Works of Emmerich.

Knapp<sup>4</sup> states that the attention of analysts should be directed to the fact that in the immediate future they will be called upon to analyze certain new artificial fats prepared by hydrogenation and, not improbably, to detect their presence as adulterants. Thus, for example, starting with olive oil, as the absorption of hydrogen proceeds, a turbid oil, then a liquid magma, then a soft fat, and finally a hard fat, is obtained. Knapp observes "A similar change occurs with all oils containing glycerides of unsaturated acids. This rise in the melting point is naturally accompanied by a decrease in the iodine value and refractive index. Fats have been prepared in this way from cottonseed oil with iodine values as low as 5, and if desired the iodine value could doubtless be reduced to 0, and the melting point raised to 60°–70° C. While it is too costly for commercial purposes to carry the saturation of the unsaturated glycerides to completion, it might be of value in the laboratory as an aid to determining the component glycerides in a pure oil. Not only the oils containing glycerides of oleic acid can be hardened, but also those containing glycerides of linolic acid and linoleic acid (the drying oils), and even of such highly

<sup>1</sup> Chem. Ztg., 1913, 58 and 369

<sup>2</sup> Ibid., 1913, 815.

<sup>3</sup> Oils, p. 4. Oil and Fat Ind., 1913, No. 14 and 15, and Seifen Ztg., 1913, 529.

<sup>4</sup> The Analyst, 1913, 102.

unsaturated acids as clupanodonic (in whale oils). Anyone who has seen a malodorous oil converted into a bland odorless tallow realizes the commercial possibilities of the process. And when it is remembered that the process can be stopped when the iodine value reaches a desired number, the possibility becomes evident of the preparation of a fat with any required analytical figures." In support of the foregoing, Knapp furnishes the following data:

Appearance.....	Original oil	Hardened oils			
	Clear liquid	Solid particles floating in oil	Soft greasy solid	Brittle solid	
Butyro-refractometer (corrected to 40° C.)....	57.7	..	..	47.7	
Fatty acids					
Iodine value.....	110	94	55	22	
Titer.....	34.7° C.	37.0° C.	42.5° C.	52.2° C.	
Neutralization value (mg. KOH).....	197	196	196	192	

The analyst is chiefly interested in the question of how these fats are to be detected. It is doubtful if their most characteristic feature, the relatively high percentage of stearic glycerides which they contain, will be of much service. Knapp states that until the manufacturer accomplishes the difficult step of completely removing the nickel, the detection of traces of this metal will be the simplest and most reliable test for hardened oils.<sup>1</sup> Although the catalyst is very finely divided, the manufacturer can obtain a perfectly clear fat by careful filtration, and hence it is the nickel contained in the nickel soaps formed by the free fatty acids present that one has to detect. The following method is suggested: 50 grams of the fat are heated in a flask with 20 cc. hydrochloric acid, with continued vigorous shaking. The mixture is allowed to separate while hot, and part of the acid solution is evaporated to dryness, dissolved in a drop of water, and placed on a white tile. One drop of ammonium sulfide is added to this and also to a drop of water for comparison. Knapp however, tried this test only on a few hardened oils, and in some cases with negative results. Dimethylglyoxime is a much more delicate test, but unfortunately Prall has found<sup>2</sup> that certain pure untreated oils give a red coloration. Hence further investigation is needed.

One of the most characteristic tests for fish oils—the bromide estimation—is quantitatively useless for these oils after hardening, as the percentage of ether-insoluble brominated glycerides is greatly reduced thereby. Not only are the analytical figures for the oils altered by this absorption of hydrogen, but also the traces of substances which often serve as a useful test for the particular oil in which they occur—*e. g.*, Halphen's reaction. Knapp believes Bomer's observation that phytosterol and cholesterol are not changed in this process is of great analytical value.

Three fats obtained by Knapp from a clear cottonseed oil, hardened by hydrogen with the help of different catalysts, gave the following figures:

<sup>1</sup> Too much reliance should not be placed on the nickel test as evidencing the presence or absence of hydrogenated oils. It is known to the writer that hardened oils which are free from nickel are on the market, these in some cases presumably having been prepared with the aid of palladium as a catalyst.

<sup>2</sup> Bomer, *Zeitsch. Untersuch. Nahr. Genussm.*, **1912**, 24, 104; and *Analyst*, **1912**, 37, 452.

Catalyst	Percentage of catalyst in oil	Character of product	Butyro-refraction (Corrected to 40° C.)	Melting point °C.
Nickel	1.00	Hard	45.7	49
Platinum.....	1.10	Hard	47.8	46
Palladium.....	0.06	Brittle	45.5	52

The keeping properties of these hardened oils were found to be remarkably good. Although prepared nearly a year and a half previously and having often been exposed to damp air, yet they showed no signs of rancidity. The free acidity (0.70 per cent as oleic acid) did not appreciably change during the period of observation.

Bomer<sup>1</sup> is in substantial agreement with the foregoing, for he states that (1) the hardened oils, as a result of the more or less complete transformation of unsaturated fatty acids (oleic, linoleic, linolenic) into stearic acid, show an increase in the melting and solidifying points as well as a lowering of the refractometer number and iodine number while the saponification number is but little altered.

(2) Judging by the iodine numbers of the liquid fatty acids, these acids appear to be not uniformly transformed into stearic acid, but the transformation of oleic acid appears to progress more slowly than the less saturated linoleic and linolenic acids, etc.

(3) Among the hardened oils, the soft and medium hard products, in color, consistency and in part also in odor and taste, show a greater or less similarity to beef or mutton tallow, so that by external appearance one cannot distinguish these hardened oils from such animal fats; for example medium hard peanut oil is so completely like neutral lard, and hardened whale oil is so like mutton tallow, that one is not able to distinguish between these fats by appearance, consistency, odor nor taste.

(4) Not only in their outward properties are these hardened oils like hog fat and mutton tallow, but also the usual analytical constants are so similar that one cannot distinguish some samples of hardened peanut oils and hardened sesame oil from hog fat, nor whale oil, in some cases, from mutton or beef tallow. In the latter case even the Polenske numbers agree while in the case of sesame oil they are somewhat lower than hog fat.

Oil	Appearance	Melting point	Solidifying point	Refractometer at 40°	Acid No. (a)	Saponification No.	Iodine No.
Peanut oil untreated	{ Yellow liquid.....	..	..	56.8	1.1	191.1	84.4
Peanut oil hardened	{ White tallowy.....	51.2	36.5	50.1	1.0	188.7	47.4
Sesame oil hardened	{ White tallowy.....	62.1	45.3	38.4(b)	4.7	188.9	25.4
Cottonseed oil hardened	{ Yellowish lard like.....	38.5	25.4	53.8	0.6	195.7	69.7
Cocoanut oil untreated	{ White soft.....	25.6	20.4	37.4	0.3	255.6	11.8
Cocoanut oil hardened	{ White lard like.....	44.5	27.7	35.9	0.4	254.1	1.0
Whale oil hardened	{ Yellowish tallowy.....	45.4	33.7	49.1	1.1	193.0	46.8

(a) Milligrams potassium hydroxide for 1 gram fat.

(b) Determined at 50° C.

Bomer examined a number of hydrogenated oils and tabulated the results of his investigations and from these the above condensed table has been compiled.

<sup>1</sup> *Chem. Rev. u. d. Fett und Harz Ind.*, **1912**, 220.

The solid and liquid fatty acids separated from the hydrogenated fat by the method of Farnsteiner showed the following properties:

Oil	Solid fatty acids		Liquid fatty acids	
	M. P.	Acid No.	Refraction at 40° C.	Iodine No.
Peanut oil untreated	..	..	47.6	91.8
Peanut oil hardened.....	..	199.7	42.9	82.9
Sesame oil hardened.....	56.4	199.5	44.7	88.9
Cottonseed oil hardened..	45.0	206.8	48.3	115.6
Whale oil hardened.....	..	199.5	44.4	96.0

Samples of these hardened oils were examined for cholesterol and phytosterol. Hardened peanut oil was found to contain 0.4 per cent, sesame oil 1.9 per cent, cottonseed oil 1.6 per cent, and whale oil 0.2 per cent of sterol, of which the three first hardened products mentioned exhibited the typical crystalline form of phytosterol. The melting point of these sterols ranged from 132 to 139° C., yielding acetates melting between about 126 and 129° C. The hardened whale oil gave a sterol melting at 149.7° C.

Bomer made a series of fractional crystallizations of hardened oil and from a sample of hydrogenated peanut oil obtained tristearine (amounting to about 2-3 per cent). Bomer has called attention to the rather striking behavior of cocoanut oil. He calculated from the iodine number that the natural oil contained 13 per cent of oleic acid and after hydrogenation approximately about 1 per cent of this acid was present. As a result of the transformation of 12 per cent of oleic acid into stearic acid, the melting point increased from 25.6° C. to 44.5° C., or thus 18.9° C., while the solidifying point advanced from 20.4° C. to 27.7° C., or only 7.3° C.

A species of hardened fish or whale oil known as "Talgit" has been examined by Müller,<sup>1</sup> who found the product to have an acid value of 12.8, an iodine number of 49 and a titer (fatty acids) of 39.4° C. The fat was saponified and pressed to obtain stearic acid. It was found that the operation of pressing could be carried out effectively to yield a product technically free from liquid fatty acids: 35 per cent of solid fatty acid having a titer of 48.7° C. was thus obtained. Müller states that since mixtures of stearic and palmitic acids possess a solidifying point above 53.5° C. the low titer of the solid acids of Talgit points to the presence of solid acids other than stearic and palmitic. Dubovitz<sup>2</sup> thinks the low melting point to be due to the presence in the original fish or whale oil of hypogaic and physetolic acid or similar acids with possibly unsaturated fatty acids of a still lower number of carbon atoms.

Leimdorfer<sup>3</sup> regards the stearine produced by the hydrogenation of some oils to be perhaps an allotropic form of natural stearine.

An attempt is made by Grimme<sup>4</sup> to identify fish oils after they have been hardened. As stated, the ordinary constants give no clue to the original source of a hardened oil and hence Grimme resorts to color re-

actions. A list of tests is given for each of the four classes of fish oils: (1) Seal oils; (2) Whale oils; (3) Liver oils; (4) Fish oils; and also characteristic tests for individual oils. These tests were also applied to two hardened oils of unknown origin and Grimme believes from his results that the color reactions are characteristic enough to establish the presence of fish oils. Nickel was found in the samples, Fortini's test (as detailed below) giving the strongest coloration. Color reactions were applied to six authentic whale oils from two different sources, and hardened to different degrees. These tests were carried out by dissolving 5 parts of the sample in 95 parts of benzene-xylene (1:1) and agitating 5 cc. of the solution with the reagent; after 5 minutes and 60 minutes the color was noted. Grimme finds the iodine-sulfuric acid reaction (1 cc. concentrated sulfuric acid and 1 drop tincture of iodine) to give a characteristic violet-red color for whale oil though the intensity of coloration decreases with increasing hardness. The constants of the six samples of hydrogenated fish and whale oils employed and the coloration produced by different reagents are tabulated by Grimme.

A draft of the Codex alimentarius Austriacus, which has been prepared by a board of prominent chemists and officials including Hefter, Wolfbauer, Fischer, Hartl and Pellischek,<sup>1</sup> embraces the subject of hydrogenated oils and it is stated that considered as a food product these oils will require further careful investigation before it is determined with certainty just what rank they will take as edible products. It is noted that the fats now offered for edible purposes are white to yellowish in color, almost odorless and tasteless. Usually the consistency lies between that of ordinary butter and hard tallow. Now and then samples are found which melt at about 60° C. and are as brittle as carnauba wax. These hard products, of course, are not intended by themselves to be used for edible purposes, but are employed to raise the melting point of soft fats. Samples of hardened peanut and sesame oil with iodine numbers reduced to 50 or lower, sometimes down to 20, have been examined. Cocoanut oil with an iodine number of 2 or even lower has been met with. The cholesterol of animal fats and the phytosterol of vegetable oils is not altered by the hydrogenation process. The hardened fats, it is stated, scarcely ever appear on the market in their true light but usually are put out under some trade name such as "Peanut-oleo," "Sesame-oleo," "Peanut-margarine," "Sesame-margarine," "Crisco," and the like.

Hardened oils examined by Aufrecht<sup>2</sup> in outward appearances resembled palm kernel oil. They were very hard and of granular fracture, were either pure white or yellowish in color. A distinct odor was perceptible on melting or heating. The taste recalled that of tallowy fats. The products were readily soluble in the usual fat solvent mediums, but the solubility in methyl and ethyl alcohol was very slight. The fats were easily saponifiable. The content of free fatty acid fluctuated between 0.51-0.83 per cent. The ash

<sup>1</sup> *Seifen Z.*, **1913**, 1876.

<sup>2</sup> *Ibid.*, **1914**, 1445.

<sup>3</sup> *Ibid.*, **1913**, 1317.

<sup>4</sup> *Chem. Rev. u. d. Fett- und Harz-Ind.*, **1913**, 129 and 185.

<sup>1</sup> *Seifen Z.*, **1913**, 1087.

<sup>2</sup> *Pharm. Ztg.*, **1912**, 876.



reacted alkaline and consisted of alkali carbonate and traces of iron oxide, but no nickel or other constituent could be detected. The following analytical results are given:

	1. Durotol (yellow)	2. Durotol (white)	3. Hydrogen- ated Tran.
Color	yellowish	white	white
Specific gravity at 15° C.	0.9252	0.9257	0.9268
Melting point °C.	46.5	46.	48.
Solidification point °C.	43.5	43.5	45.5
Viscosity at 50° C.	5.4	5.4	5.6
Acid No. (calculated as oleic acid)	0.51	0.57	0.83
Saponification No.	162.2	161.	173.5
Unsaponifiable matter (per cent)	1.92	2.1	2.4
Acetyl No.	1.2	1.2	0.95
Iodine No.	3.9	4.2	7.8
Hehner No.	95.8	95.8	96.4
Reichert-Meißl No.	0.38	0.36	0.52
Water.	0.	0.	0.
Ash.	0.037	0.03	0.05

The detection of traces of nickel by the usual analytical methods is often difficult. Dimethylglyoxime, proposed by Tchugaeff, is a reagent of great sensitivity. Its application has been investigated by a number of chemists, and among these Bianchi and DiNola<sup>1</sup> report that the presence of copper and iron interferes with the test. They worked with an acid reagent and used the following procedure:

To the substance supposed to contain nickel one or two drops of concentrated hydrochloric or nitric acid are added and the acid solution so obtained is placed in a porcelain dish, or preferably on a strip of filter paper. A few drops of ammonia are added, or in case the strip of filter paper is used, this may simply be exposed to the vapors of ammonia. The liquid is acidified with acetic acid and a drop of concentrated alcoholic solution of dimethylglyoxime is added. The presence of nickel is shown by a red coloration which grows more pronounced in the course of time. This reaction is a very simple one and does not require any particular technical knowledge for carrying out.

Fortini<sup>2</sup> has simplified this reaction and uses an alkaline instead of an acid reagent which apparently gives more satisfactory results than the above procedure. Fortini mixes one-half gram of dimethylglyoxime, 5 cc. 98 per cent alcohol, and 5 cc. concentrated ammonium hydroxide in the order as given, yielding a clear, faintly yellowish liquid which in glass-stoppered bottles may be kept for a long time unchanged. The test is carried out as follows:

The sample to be examined is freed from fat by extraction with ether and to the residue a drop of the reagent is added. When nickel is present there will appear in a few seconds a rose colored flock caused by reaction with the nickel oxide present on the surface of the metallic nickel. Of course, if nickel is present in the form of a soap, the fat should be extracted with, for example, aqueous hydrochloric acid in the manner prescribed by Knapp in the foregoing. In order to make the reaction even more sensitive, the residue may be heated for a few moments in an oxidizing flame to produce nickel oxide.

The detection and determination of small quantities

of nickel by  $\alpha$ -benzildioxime is described by Attack<sup>1</sup> as follows:

An alcoholic solution of  $\alpha$ -benzildioxime gives with nickel compounds a bulky red precipitate which is insoluble in water, alcohol, acetone, 10 per cent acetic acid, and ammonia; the precipitate becomes reddish yellow on boiling. The reagent is much more sensitive than dimethylglyoxime, showing 1 part of nickel in 5 million of water, and the precipitate is readily filtered.<sup>2</sup> Small quantities of nickel are determined as follows: 150 cc. of a hot saturated alcoholic solution of the oxime are added for every 0.01 gram of nickel, the mixture is heated for a few minutes on the water-bath, filtered, the precipitate washed with hot alcohol, and dried at 110°–112° C.; it has the formula  $C_{28}H_{28}N_4O_4Ni$  and contains 10.93 per cent Ni. Nickel may be separated from cobalt in ammoniacal solution.  $\alpha$ -Benzildioxime is prepared by boiling 10 grams of benzil, dissolved in 50 cc. of methyl alcohol, with a concentrated aqueous solution of 8 grams of hydroxylamine hydrochloride, for 6 hours, washing the precipitate with hot water and then with a small quantity of ethyl alcohol, in which it is only slightly soluble. It may be crystallized from acetone.

The hydrogen value is proposed by Fokin<sup>3</sup> as a means of determining unsaturated organic compounds in a manner similar to the iodine values of Hubl and Wijs.

The "hydrogen value" of an organic compound is defined as the number of cubic centimeters of hydrogen (at 0° and 760 mm.), which are absorbed by 1 gram of the compound. For the test, an apparatus is devised consisting of a distillation flask (50–150 cc.) having a small beaker fused inside on the bottom, and connected by means of the side-tube to a gas burette and a gasometer containing hydrogen. In the small beaker are placed about 0.1 gram of catalytic platinum, moistened with  $\frac{1}{2}$  cc. of water, and in the flask the substance to be examined and 20–30 cc. of alcohol free from dissolved oxygen. Hydrogen is admitted and the flask is shaken by a shaking machine until absorption is complete. The following hydrogen values were obtained by Fokin, the figures in parentheses being either the hydrogen values corresponding with Wijs' iodine value, or, where indicated, the theoretical hydrogen values. Elaidic acid, 78.6–81.4 (78.8); oleic acid, 86.2–87.2 (86.2); fatty acids from sunflower oil, 119.6–120.8 (122.9); fatty acids from linseed oil, 164.9–166.3 (166.0); castor oil, 73.7 (75.5); Croton oil, 260.9 (theoretical, 258.4); undecic acid, 115.6 (114.1); erucic acid, 39.4 (65.6). Colorophony does not absorb hydrogen under the conditions of the test. The "hydrogen value" of course is not a determination as yet of use in the identification of hardened oils, but is noted here because of its incidental interest.

The foregoing embraces most of the information available from published sources on the analytical side of hydrogenated or hardened oils and it is hoped that the very meagreness of the data may serve as a stimulus

<sup>1</sup> Chem. Ztg., 1913, 37, 773.

<sup>2</sup> Compare Ibbotson; J. S. C. I., 1911, 1317.

<sup>3</sup> J. Russ. Phys. Chem. Soc., 40 (1908), 700, J. Chem. Soc., 1908, 94 (1908), II, 637.

<sup>1</sup> Boll. Chim. Farm., 1910, 517.

<sup>2</sup> Chem. Ztg., 1912, 1461.

for abundant investigations tending to clarify the subject and enabling fairly definite procedures to be adopted for the qualitative and quantitative examination of these products.

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## THE CHEMISTRY AND PROPERTIES OF GLYCERO-PHOSPHATES (GLYCERINOPHOSPHATES)

By GASTON DU BOIS

Received October 16, 1913

In an article on "Calcium Glycerophosphate," which appeared in two numbers of the *Journal de Pharmacie et de Chimie* of May 1 and 16, 1913, the authors, E. François and E. Boismenu, start their critical review of the literature on glycerophosphates by pointing to the great number of publications on the subject.

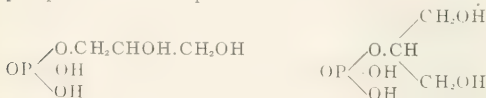
They believe that in spite of the comparatively voluminous literature few of those interested in this subject can draw exact conclusions from those publications as to the nature or composition of synthetic glycerophosphates and of the products found on the market.

In the literature including the leading authoritative publications on organic chemistry we find such contradictory statements as to make it impossible for any one unfamiliar with the subject to recognize which are correct.

The writer having had some experience in the manufacture of glycerophosphates, and having, therefore, spent some time studying the chemistry of these products, deemed it advisable to collect the most important known facts on the subject and to endeavor to draw conclusions by adding his experience to that gathered from the research work of others, and also to point out a few of the erroneous statements and inconsistencies found in some publications.

Before going into the details of the chemistry and properties of glycerophosphates, and the findings of the various chemists who have developed this field, let us briefly examine what compounds are theoretically possible as a result of the action of phosphoric acid or its salts, on glycerine.

By the interaction of 1 molecule phosphoric acid with one molecule glycerine, two isomeric monoglycerophosphoric acids are possible.

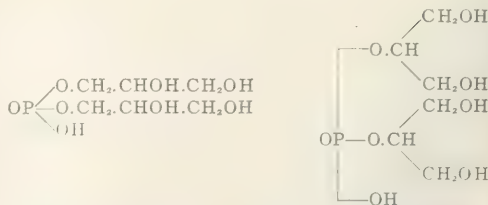


1.  $\alpha$  monoglycerophosphoric acid

2.  $\beta$  monoglycerophosphoric acid

These acids can form mono- and dibasic salts. The dibasic calcium salts of above acids are the main components of calcium glycerophosphate of the market.

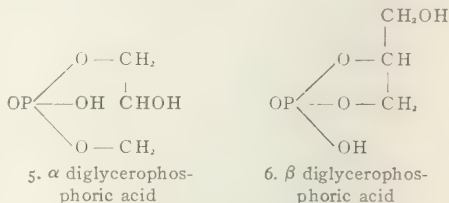
If one molecule phosphoric acid interacts with two molecules glycerine, again two isomeric diglycerophosphoric acids are possible:



3.  $\alpha$  diglycerophosphoric acid

4.  $\beta$  diglycerophosphoric acid

Some authors claim diglycerophosphoric acids to have the following constitution:<sup>1</sup>



5.  $\alpha$  diglycerophosphoric acid

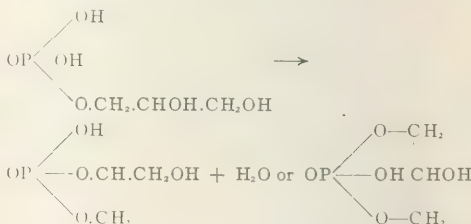
6.  $\beta$  diglycerophosphoric acid

The diglycerophosphoric acids, whatever their constitution may be, can form only monobasic salts. The salts of these acids are readily partly saponified by the action of alkali hydroxides yielding mainly monoglycerophosphates.

Diglycerophosphoric acids are formed when phosphoric acid is mixed with glycerine, preferably an excess of the latter, and the mixture heated to above  $110^\circ$  under reduced or atmospheric pressure. The formation of diglycerides at temperatures above  $110^\circ$  was demonstrated very conclusively by Adrian and Trillat,<sup>2</sup> by Power and Tutin,<sup>3</sup> and also by Carré.<sup>4</sup>

The question, which are the correct formulas for the  $\alpha$  and  $\beta$  diglycerophosphoric acids, formulas 3 and 4 or 5 and 6 is not settled yet. Adrian and Trillat analyzed diglycerophosphoric acid and obtained figures for C and H corresponding about with the amount contained in formulas 3 and 4.

It is possible that both are correct as it is reasonable to expect that monoglycerophosphoric acid when heated could, by the elimination of water, form diglycerophosphoric acid:



We now come to the last class of esters formed

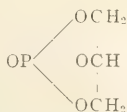
<sup>1</sup> Carré, *C. r. de l'Acad. des Sciences*, **137**, 1050-73, also **138**, 47-49.

<sup>2</sup> *J. Phar. et Ch.*, [6] **7**, 226-30.

<sup>3</sup> Power and Tutin, *J. Chem. Soc.*, **87**, 240-57.

<sup>4</sup> Carré, *C. r. de l'Acad. des Sciences*, **137**, 1070-73.

by the action of phosphoric acid on glycerine, the triglycerophosphoric ester. This compound has the following formula:



It is, according to Carré, insoluble in water, alcohol and acetone, and forms a hard, spongy mass which can be powdered.

It is interesting to note from the following example the relative amounts of mono, di and tri esters formed under various conditions, which is shown in the following table taken from G. Prunier's investigations.

Equal amounts of 60 per cent phosphoric acid and glycerine 28° B. were heated together under atmospheric pressure.

Temp.	Hours heated	Monoether	Diether	Triether	Total
110°	72	39.3	37.4	0.6	77.3
110°	84	43.9	33.5	0.6	78.0
130°	12	36.8	29.0	0.6	66.4
130°	24	36.1	27.1	1.9	65.1

Equally interesting is the result of investigations by G. Prunier<sup>1</sup> on the rate and limit of esterification of phosphoric acid by glycerine under varying conditions of concentration, temperature and pressure.

The investigation shows that the best results are obtained if the water formed during the reaction is eliminated, which can best be attained, either by heating the reaction mixture under reduced pressure or by exposing a comparatively large evaporating surface. The limit of esterification under reduced pressure appears to be reached when 80 per cent of the acid is esterified and this point is arrived at more quickly at higher temperatures, 24 hours being required at 110°, 12 hours at 130° and 8 hours at 150°. Under atmospheric pressure the speed of esterification also increases with higher temperatures, but the limit of esterification decreases. For example with 85 per cent acid and glycerine 30° B. at 110° the limit of esterification is 75.8 per cent but drops to 60.9 per cent at 130° and to 49.4 per cent at 150°. Under atmospheric pressure the best results for the esterification are obtained at 110° and by using 60 per cent phosphoric acid and glycerine 30° B. whereby 78 per cent of the acid is esterified.

At higher temperatures and under reduced pressure the chief product is the diester, this being replaced, in part by the monoester when esterification is slow (namely, at higher pressures and lower temperatures) and by the triester when the operation is conducted at a still higher temperature.

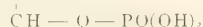
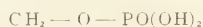
Regarding the stability of glycerophosphoric acid or in other words its velocity of hydrolysis, F. Malengreau and G. Prigent<sup>2</sup> found that the decomposition of glycerophosphoric acid is a case of autocatalysis, caused by the action of the uncombined acid groups

of the phosphoric acid, as when these are neutralized the decomposition at 100° is practically reduced to zero. With rising temperature the hydrolysis is notably accelerated. There is a certain acidity or concentration of H ions above and below which the stability of the compound increases. This explains why strong acids, such as HCl, H<sub>2</sub>SO<sub>4</sub>, acetic acid, etc., retard the decomposition owing to the increase in the concentration of the H ions in the solution. On the other hand weak acids such as oxalic and citric acids and their salts accelerate the hydrolysis of glycerophosphoric acid. The degree of acidity at which the hydrolysis is the greatest is represented by acid salts of glycerophosphoric acid.

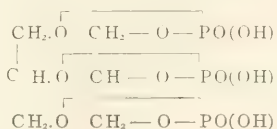
The potassium salt decomposes more rapidly than the calcium and sodium salts. The salts of strong acids have mostly but a slightly accelerating effect but the salts of weak acids accelerate the hydrolysis reaction considerably.

Before leaving the subject of the possible compounds resulting from the esterification of phosphoric acid by glycerine, the investigations by A. Contardi, recently published should be briefly mentioned.<sup>1</sup>

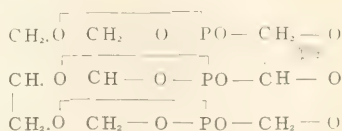
By heating at 120–130° three molecules crystallized phosphoric acid under reduced pressure with one molecule glycerine, *glycerotriphosphoric acid* is obtained:



This triphosphoric ester heated with one molecule glycerine yields *diglycerotriphosphoric ester*:



which compound yields when again heated with one more molecule glycerine the neutral triglycerotriphosphoric ester:



This compound is identical with Carré's triglycerotriphosphoric ester

phosphoric ester  $\text{CH} - \text{O} - \text{PO}$ , the latter being just one-third of the formula proposed by Contardi.

The correctness of Contardi's formula for triglycerotriphosphoric ester has not yet been proved owing to

<sup>1</sup> Bull. de la Soc. Chim. de France, 1907, [4] 1, 1046–48.

<sup>2</sup> Z. physiol. Chem., 1911, 73, 68–84.

<sup>1</sup> Gazz. Chim. Ital., 42, II, 270–82.



the insolubility of this compound, which makes it impossible to determine the molecular weight.

P. Carré does not agree with Contardi's findings;<sup>1</sup> the question of the existence of above compounds is, therefore, not definitely settled.

In contrast to the methods used by all of the above mentioned authors for synthesizing glycerophosphoric esters, I find that the present manufacturing methods, judging from the patent literature, start not from phosphoric acid, but mostly from mono- and dibasic salts of ortho- or metaphosphoric acids. One patent describes the use of a mixture of metaphosphoric acid, disodium phosphate and glycerine; another patent covers the use of monosodium phosphate and glycerine, etc.

The purpose of deviating from the original method of Pelouze (phosphoric acid and glycerine) is partly in order to prevent the formation of triglyceroesters, by protecting one of the acid groups by a base, and partly for other practical reasons which do not enter into the subject of this paper.

We now come to the examination of the principal salts of glycerophosphoric acid found on the market, the calcium, sodium and potassium glycerophosphates.

**CALCIUM GLYCEROPHOSPHATE.**—An examination of various market products which I carried out in our laboratories showed how widely these products differ in composition.

Sample	H <sub>2</sub> O of crysts. and moisture	Based on anhydrous product				Added org. acid fig. as citric
		Ash	CaO	P <sub>2</sub> O <sub>5</sub>	Titration	
1.....	10.03	55.32	19.23	32.03	56.1%	-
2.....	9.44	50.94	22.70	28.15	80.7%	7%
3.....	8.79	54.66	24.45	29.58	85.3%	5%
4.....	10.39	56.35	22.2	33.68	71.0%	-
5.....	12.73	59.02	26.56	31.9	...	-
L. P. 6	1.25	60.12	26.96	34.77	99.39	-
Theory.....	7.89	60.47	26.68	33.80	100.0%	-

Sample No. 6 was a laboratory preparation almost free of water.

From the above figures we find the moisture in the products varying from 8.79–12.73 per cent, the ash from 50.93–59.02 per cent, CaO from 19.23–26.56 per cent, P<sub>2</sub>O<sub>5</sub> from 28.15–33.68 per cent. All of the figures for ash, CaO, P<sub>2</sub>O<sub>5</sub> being based on dry substance.

If we compare their solubilities we find still greater differences and it is, therefore, evident that these products must differ widely from one another.

G. Prunier examined samples which showed solubilities in water ranging from 1:11 up to 1:60 parts of water.

The causes for these divergences are mainly:

1. The presence of organic acids (citric acid, etc.) which increase the solubility.
2. The presence of diglycerophosphates which also increase the solubility.
3. Different mixtures of  $\alpha$  and  $\beta$  glycerophosphates the  $\beta$  glycerophosphate being less soluble than the  $\alpha$  isomeride.

The two first causes will not be discussed in this paper as organic acids or diglycerides are impurities added for the purpose of apparently increasing the

solubility. That the solubility is mostly only apparently increased is explained by the fact that although such products will at first readily dissolve in 25–40 parts of water, on longer standing, however, calcium citrate will gradually be formed and precipitate out of the solution and in the case of diglycerides being present, they will slowly hydrolyze forming monoglycerophosphates and also some free phosphoric acid. Furthermore, as is shown in this paper, the presence of organic acids (weak acids) or their salts will increase the hydrolysis of monoglycerophosphates, thereby causing CaHPO<sub>4</sub> to be formed.

The mistake has been repeatedly made by various authors in determining the solubility of pure calcium glycerophosphate, not to take into consideration the fact that the products examined may have contained one or the other of the two possible isomerides or even a mixture of both of these, and the result, naturally, has been that very widely differing statements were made concerning the solubility of these products.

Tutin and Hann in an endeavor to finally ascertain the nature of the natural and synthetical<sup>1</sup> glycerophosphoric acids, have prepared these products and their barium salts and also the  $\alpha$  and  $\beta$  monoglycerophosphoric acids separately and their barium salts under such conditions as they hoped would exclude the formation of other products.

As the determination of the properties of the  $\alpha$  and  $\beta$  isomerides is of the utmost importance as a basis for a thorough knowledge of the composition of commercial products and of the requirements to be established for such products, the writer will briefly discuss a part of Tutin and Hann's work and results. This appears all the more necessary in view of the importance of their researches and because their findings regarding the solubility of a barium glycerophosphate as well as that of the synthetical product do not coincide with the results of more recent investigations.

Tutin and Hann prepared  $\alpha$  barium glycerophosphate by chlorinating dry allyl alcohol and thereby producing  $\beta$  dichlorhydrin, which was heated with one and a half molecules of crystallized phosphoric acid at a temperature of 150–155°. The product obtained was boiled with milk of lime and the  $\alpha$ -calcium glycerophosphate thereby obtained, converted into the barium salt.

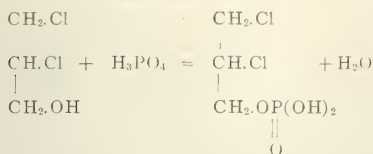
It should be noted that the yield in the esterification of  $\beta$  dichlorhydrin with phosphoric acid is small and that furthermore, the heating of the mixture at 155° for several hours does not exclude the possibility of HCl being driven off, whereby phosphoric acid would combine with glycerine allowing the formation of  $\beta$  glyceric- or diglycerophosphates, or even glycerodiphosphoric esters.

In connection with the above method of preparing  $\alpha$  calcium glycerophosphate, it is interesting to compare the Eng. Pat. 2883, whereby monochlorhydrin or monoacetin is heated with syrupy phosphoric acid until no more hydrochloric acid or acetic acid is evolved.

<sup>1</sup> By synthetical glycerophosphoric acid is meant the product obtained by heating glycerine and phosphoric acid for 24 hours at 105–110° C.

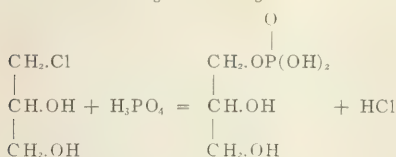
We find here an attempt to produce the esterification by introducing phosphoric acid in the position occupied by the chlorine in monochlorhydrin whereas Tutin and Hann did just the opposite; they intended to introduce phosphoric acid in the only remaining hydroxyl group of  $\beta$  dichlorhydrin leaving the chlorine groups intact.

*Tutin and Hann*



$\beta$  dichlorhydrin

*Eng. Pat. 2883*



$\alpha$  monochlorhydrin

In view of the above, I am of the opinion that the figure obtained by Tutin and Hann for  $\alpha$  barium glycerophosphate, soluble 1 : 26.6/17°, cannot be accepted as final. This figure does not correspond with the solubility determined quite recently by Langheld, Oppmann and Meyer,<sup>1</sup> which they found to be 1 : 11.9.

The solubility 1 : 53.7, found by Tutin and Hann for the synthetical barium glycerophosphate, obtained by heating glycerine and phosphoric acid for 24 hours at 105–110°, is also so far off from the solubility of  $\alpha$  barium glycerophosphate that their result would apparently require confirmation.

I compare in the preceding paragraph the synthetical barium glycerophosphate, obtained by Tutin and Hann, with the  $\alpha$  barium glycerophosphate obtained by Langheld, Oppmann and Meyer. This comparison is justifiable as the two products should be almost identical. The main product of esterification of glycerine by phosphoric acid under the conditions as carried out by Tutin and Hann, is the  $\alpha$ -isomeride. This corresponds to the fact that when glycerine is treated with an equivalent amount of hydrochloric acid,  $\alpha$  chlorhydrin is the chief product obtained, only a small amount of  $\beta$  chlorhydrin being formed.

We find that in all cases in which mono esters of glycerine are formed at low temperatures, by the interaction of acids or their salts on glycerine, the  $\alpha$  isomeride is the chief product of the reaction.

If the solubility of synthetical barium glycerophosphate of 1 : 53.7 found by Tutin and Hann were correct, this barium compound would then be less soluble than the corresponding synthetical calcium glycerophosphate, the solubility of which was determined by Power and Tutin and also by Adrian and Trillat.

Synthetic

Ca glycerophosphate...	1 : 23.4/16°	Power and Tutin
Ca glycerophosphate...	1 : 22.0/25°	Adrian and Trillat

I find, however, that the barium glycerophosphates are more soluble than their corresponding calcium salts. Let us for instance compare the solubilities of the barium and calcium salts prepared from crystallized sodium glycerophosphate, which latter product was prepared for the first time about seven years ago and has since been examined very carefully by various authors and recognized as pure  $\beta$  sodium monoglycerophosphate.

$\beta$ Ca glycerophosphate...	1 : 59.5/18°	Rogier and Fiore
$\beta$ Ca glycerophosphate...	1 : 77 : 15°	Paolini
$\beta$ Ba glycerophosphate...	1 : 22.2/21°	Rogier and Fiore
$\beta$ Ba glycerophosphate...	1 : 36.8/17°	Tutin and Hann

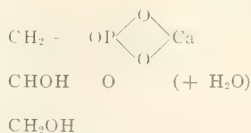
If we admit that the synthetical calcium glycerophosphate prepared as above described, contains mostly the  $\alpha$  isomeride, we can conclude that the solubility of  $\alpha$  calcium glycerophosphate in water must be about 1 : 22/16°, and that the solubility of the  $\alpha$  barium glycerophosphate is greater than that of the calcium salt or as found by Langheld, Oppmann and Meyer, 1 : 11.9/22°, which, as these authors remark, corresponds very closely to the figure obtained by Tutin and Hann for barium glycerophosphate produced from lecithin, the solubility of which they found to be 1 : 13.9.

The foregoing leads forcibly to the conclusion that the synthetical glycerophosphates produced at low temperatures (100–110°), and the natural glycerophosphates obtained from lecithin are almost identical, and in all probability, a mixture of the  $\alpha$  and  $\beta$  isomerides, in which the  $\alpha$  isomeride predominates.

By eliminating the statements, which by their contradictory nature and inconsistency have tended so far to obscure the true knowledge of the chemistry and properties of glycerophosphates, and by condensing from the foregoing the actual facts, we come to the following description of the principal salts of glycerophosphoric acid:

CALCIUM MONOGLYCEROPHOSPHATE. Both the  $\alpha$  and  $\beta$  isomerides are known.

$\alpha$  CALCIUM GLYCEROPHOSPHATE is a white amorphous or crystalline powder of the following formula:



When precipitated from a cold, saturated, aqueous solution, by prolonged heating on the water bath, it separates as a fine crystalline powder, which after drying at 70° C. is practically anhydrous.

When precipitated out of a cold aqueous solution by the addition of alcohol, it forms an apparently amorphous precipitate which on drying below 70° C. retains one molecule of water; when, however, it is precipitated from the solution of its corresponding sodium salt, by the addition of  $\text{CaCl}_2$ , it forms a crys-

<sup>1</sup> Ber. d. chem. Ges., 45, 3757 (1912).

<sup>2</sup> J. Chem. Soc. Transactions, 89, 249–57.

talline precipitate, containing one molecule of water of crystallization, which is not driven off when the product is dried below 70° C. Both products are hygroscopic.

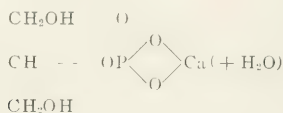
Anhydrous  $\alpha$  calcium glycerophosphate is soluble in about 22 parts of water at 20° C., and precipitates out on heating, being soluble only in 108 parts of water at 100°.

It is insoluble in alcohol.

It is neutral or very slightly alkaline towards phenolphthalein; on addition of one equivalent of acid, the acid salt is obtained which is neutral towards methyl orange.

The dry salt contains 26.68 per cent CaO and 33.80 per cent  $P_2O_5$  and yields on incineration 60.47 per cent ash.

$\beta$  CALCIUM GLYCEROPHOSPHATE is much less soluble than the  $\alpha$  isomeride; it dissolves in about 60 parts of water at 20° C. It is obtainable as a crystalline or amorphous precipitate under the same conditions as were enumerated for the  $\alpha$  isomeride. It has the following formula:



COMMERCIAL CALCIUM GLYCEROPHOSPHATE is a mixture of the two above described isomerides; therefore, no specific solubility can be given for this mixture. It is evident that very different results will be obtained if the solubility of such a mixture is determined by shaking an excess of the product with water and determining the amount of substance dissolved in a weighed amount of water, or whether the solubility is determined by adding to a weighed amount of the product barely as much water as is required to produce a clear solution. The first method is naturally worthless in this case, whereas the second method gives us the actual solubility.

Commercial products should dissolve in 40 to 50 parts of water at 20° C. For the rapid estimation and comparison of market products I would recommend the following tests:

**Moisture Determination.**—Dry the product at 120–130° C. or better still at 100° C., but under reduced pressure, to constant weight.

**Titration.**—If the product is acid towards phenolphthalein, 2 grams of the dried substance in 100 cc. of water are titrated with  $N/2$  NaOH (determination of organic acids).

If the product is neutral or very slightly alkaline towards phenolphthalein, 2 grams in 100 cc. of water are titrated with  $N/2$  HCl using methyl orange as indicator; 1 cc.  $N/2$  HCl equals 0.105 gram calcium glycerophosphate. Although the titration is not an exact determination, still it is a convenient method for the rough estimation of calcium monoglycerophosphate.

If diglycerides are present, the titration will yield

low results indicating, in some cases, the presence of 10 per cent or more diglycerides.

**Ash Determination** is made by very slow and careful incineration of 0.5 gram dried substance, until a white ash is obtained.

A low ash percentage indicates the presence of organic acids and other organic impurities including diglycerides. A high ash percentage indicates the presence of inorganic salts, such as chlorides, sulfates, phosphates.

Further qualitative and, if necessary, quantitative determinations of such impurities as chlorides, sulfates and phosphates complete the preliminary examination of the product.

**SODIUM MONOGLYCEROPHOSPHATE.** Up to a few years ago, sodium glycerophosphate was known only in form of a syrupy liquid, or as a very hygroscopic white powder. The crystalline sodium glycerophosphate was discovered by a chemist of the Soc. Anon. des Etabl. Poulenc Frères, and the formation of this product was evidently due to a change made at the time in their method of manufacture.

V. Paolini, who was the first to publish results of investigations of this crystalline product,<sup>1</sup> found that it was pure disodium monoglycerophosphate and concluded that it was the  $\beta$  isomeride. This explains why it could be obtained in a crystalline form, whereas the products obtained by the interaction of glycerine and phosphoric acid at temperatures below 110° C., after conversion into the sodium salt, had never been known to crystallize, which can be explained by the fact that in this case, principally the  $\alpha$  isomeride is formed.

In the early part of 1912, I analyzed sodium glycerophosphate, which, for purposes of purification, I recrystallized several times, and found

	Per cent
Water.....	31.2
Sod. monoglycerophosphate.....	68.9 by titration
Sod monoglycerophosphate.....	68.5 by gravimetric $P_2O_5$ determination

Conflicting statements are found throughout the literature concerning the water of crystallization in sodium glycerophosphate; some authors give it as 1, some as 3, and again others as 7 molecules.

I found that the crystalline product contained 5 $\frac{1}{2}$  molecules of water, for which the following theoretical figures would correspond:

H <sub>2</sub> O.....	31.41%
Sod. glycerophosphate.....	68.59%

these correspond very closely to our analysis figures (given above).

My views in this matter were confirmed by a publication by V. Paolini,<sup>2</sup> which appeared a few months later, in which the author having examined samples of four different sources, found them also to contain 5 $\frac{1}{2}$  molecules of water of crystallization.

$\alpha$  SODIUM MONOGLYCEROPHOSPHATE is obtainable as a colorless or slightly yellow syrupy liquid which,

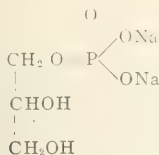
<sup>1</sup> V. Paolini, *Atti R. Accad. dei Lincei, Roma*, 1911, 20, I, 807–12 and also from same publication, 1912, 21, II, 330–52.

<sup>2</sup> *Atti R. Accad. dei Lincei, Roma*, 1912, 21, II, 350–52.



when dried completely under reduced pressure, forms a white porous mass which can be powdered but is very hygroscopic.

It has the following formula:



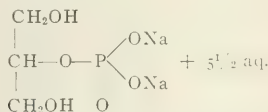
It mixes with water in all proportions but is practically insoluble in alcohol.

It is slightly alkaline to phenolphthalein and on addition of one equivalent amount of acid to its aqueous solution, the acid salt is obtained which is neutral to methyl orange.

Its solution can be heated up to 120° without decomposing.

$\beta$  SODIUM MONOGLYCEROPHOSPHATE is obtainable in form of colorless or white monoclinic crystals, containing  $5\frac{1}{2}$  molecules of water of crystallization.

It has the following formula:



It is easily soluble in water; a saturated water solution at 20° C. contains about 40 per cent of the salt.

In the form of large crystals, this salt is, at 15°, stable when exposed to the air, whereas when finely powdered and exposed to the air it effloresces. This explains why the fine sodium glycerophosphate crystals found on the market contain usually more anhydrous sodium glycerophosphate than corresponds to a salt containing  $5\frac{1}{2}$  molecules of water.

COMMERCIAL SODIUM GLYCEROPHOSPHATE.—The products that have been sold under the name of "sodium glycerophosphate 50 per cent" or "75 per cent" and also "about 100 per cent" which I have had the opportunity to examine, showed a surprising lack of uniformity in strength as well as purity.

Most of these products were in form of a syrupy liquid. It is of course impossible to produce a 75 per cent or even 50 per cent solution of  $\beta$  sodium glycerophosphate, as we have just seen that a saturated solution contains only about 40 per cent  $\beta$  sodium glycerophosphate crystals.

The liquid market products are composed of mixtures in which therefore mostly the  $\alpha$  sodium glycerophosphate predominates.

Some manufacturers in determining the strength of their products have been guided merely by the specific gravity, others evidently have determined the strength on the basis of a variable amount of water of crystallization which, of course, accounts partly for the lack of uniformity in strength.

A 75 per cent solution, containing 75 per cent sodium glycerophosphate +  $5\frac{1}{2}$  aq. is a syrupy liquid, which

mixes readily with water and is, therefore, quite convenient for use.

A preparation containing 75 per cent *anhydrous* sodium glycerophosphate, however, although it mixes in all proportions with water, has the great inconvenience of dissolving very slowly in cold water, and requiring many hours' stirring before complete solution is obtained. Even when heated the product does not dissolve readily.

I am, therefore, of the opinion that, for the sake of uniformity and convenience in handling, it should be required that the strength of the product be figured on the basis of its contents in sodium glycerophosphate +  $5\frac{1}{2}$  aq. and this basis being admitted, a 75 per cent solution would unquestionably be the most desirable form for the consumer, if he must have a liquid preparation.

The last but not least interesting form in which sodium glycerophosphate is found on the market is the crystal form, which in itself is the best guarantee of its purity and, therefore, is preferable to all other forms wherever purity is of paramount importance.

The strength of the various sodium glycerophosphates can readily be determined by titration. This method yields for pure products checking results with the gravimetric method ( $\text{P}_2\text{O}_5$  determination). It is carried out as follows:

*Titration.*—2-4 grams of the product accurately weighed are dissolved in 100 cc. of water and titrated with  $N/2$  HCl, using methyl orange as indicator.

One cc.  $N/2$  HCl equals 0.1576 gram monosodium glycerophosphate +  $5\frac{1}{2}$  aq.

The product should also be tested for sulfates, chlorides and carbonates, which are almost invariably present in the liquid preparations but should not be present in the crystals.

The products should not contain any phosphates.

POTASSIUM GLYCEROPHOSPHATE.—Both  $\alpha$  and  $\beta$  isomerides are obtainable as a colorless or slightly yellow syrupy liquid. When dried completely under reduced pressure a porous and very hygroscopic mass is obtained.

Potassium glycerophosphate mixes readily in all proportions with water. The product has never been obtained in crystal form in either of its modifications ( $\alpha$  and  $\beta$ ).

COMMERCIAL POTASSIUM GLYCEROPHOSPHATE.—This product is known mostly in form of 50 per cent and 75 per cent solutions.

Some manufacturers figure the contents on the basis of potassium glycerophosphate plus a certain amount of water of crystallization. I can see no reason for doing this as the product has never been obtained in crystal form. The only logical way of figuring the contents is on the basis of anhydrous potassium glycerophosphate.

These market products are best tested exactly as described for the sodium salts, whereby in the titration, 1 cc.  $N/2$  HCl equals 0.124 gram potassium glycerophosphate.

Concluding, I wish to emphasize that while I believe the above data embodies the most important

investigations on the chemistry of glycerophosphates, and resulting conclusions, yet I fully realize that much remains to be done in order to define, without a doubt, the characteristics of the various isomeric glycerophosphoric esters, which naturally can be achieved only after the various compounds shall have been synthesized in such a way as to exclude the possibility of other compounds being formed.

Until such time the figures given for the solubilities, for instance, must be regarded only as tentative.

LABORATORIES OF THE MOSSINGHO CHEMICAL WORKS  
ST. LOUIS, MISSOURI

### TOXICITY OF VARIOUS WOOD PRESERVATIVES<sup>1</sup>

By C. J. HUMPHREY AND RUTH M. FLEMING

Received January 8, 1914

During the past three years the writers have been conducting toxicity tests at the Forest Products Laboratory, Madison, Wisconsin, on various wood preservatives. These tests have been limited to substances in actual use in the industry or to those compounds submitted by coöperators as having a possible preservative value.

The toxicity of a given substance is not necessarily an ultimate criterion of its service value, but when correlated with other suitable properties, such as cost, ease of injection, permanence, non-corrosive action on metals and wood, fire resistance, and ease and safety in handling it assumes high importance in influencing our judgment as to what may normally be expected from the substance.

The writers have confined their attention to toxicity only, and with the view of bringing the essential data to the attention of the industry the more important results of our investigations to date are here presented.

While we are attacking the problem from two angles, namely, by the quick method of mixing the preservative with agar culture media and inoculating with fungi, and by the slower and probably more conclusive method of testing small injected wood blocks, the present paper will consider only the former, as the latter work is not yet far enough along to report upon.

Our method is essentially this: Agar culture media of the following formula is prepared:

Extract of 1 lb. lean beef in 1000 cc. distilled water.  
25 grams Loddhuns malt extract  
20 grams agar-agar.  
(Carefully filtered but reaction not adjusted; slightly acid.)

Seventeen cc. of this medium are measured out into 50 cc. glass-stoppered bottles, using a specially graduated 17 cc. pipette, the bottles then being placed in clamp-frames and sterilized with steam at 100° C. for 25, 20 and 20 minutes, respectively, on three successive days.

The handling of the preservatives involved slight modifications for individual cases, but in all instances the concentrations reported are based on the actual weight of preservative in 20 cc. agar-preservative mixture. The character of the substance determined the method of introducing it into the agar medium.

With inorganic salts soluble in water, from 3 to 10 per cent solutions (grams per 100 cc. solution) were prepared and measured out into 50 cc. glass-

stopped bottles from either a 10 or 25 cc. standardized burette graduated in  $\frac{1}{20}$  or  $\frac{1}{10}$  cc., respectively. To each bottle sufficient distilled water was added to make 3 cc.

All other preservatives were weighed out into similar bottles on an analytical balance, and distilled water likewise added to make 3 cc. In the case of certain thick viscous oils, namely, wood tar, wood creosote, coal tar creosote and its fifth fraction, which do not readily emulsify with water, 5 to 33 $\frac{1}{3}$  per cent stock emulsions were prepared, using equal amounts of gum arabic and preservative and diluting with water to the desired concentration; these emulsions were then used in place of the crude preservative.

In a few instances where the preservatives were very low in toxic properties, more than the specified 3 cc. were necessary in order to secure the higher concentrations, and in these cases it became necessary to take into consideration the excess of preservative and to reduce the amount of agar by just this amount in order that the combined volume might not exceed 20 cc.

After the preservative had been introduced into the bottles as indicated, the stoppers were sealed in with a rubber-glycerine burette cock grease and the bottles were then sterilized along with the agar containers.

After sterilization both agar and preservative were heated on the water bath and the former was poured into the preservative bottle in a sterile culture box, thoroughly shaken, and then poured into sterile petri dishes 100 mm. in diameter and 10 mm. deep. After cooling, the surface of the medium was inoculated at the center with a weft of fungus mycelium 5 to 6 mm. square cut from a petri dish culture 2 to 3 weeks old. The test dishes thus prepared were then placed in an incubator and held at approximately 25° C. for from 4 to 10 weeks, usually 4 to 6. For each set of concentrations a check culture, using 17 cc. agar media plus 3 cc. of distilled water, was prepared.

The method as above outlined is not, by any means, intended to furnish the last word on the toxicity of a preservative, but it has the advantage of being quickly and easily applied and gives us at least valuable indications. The principal objection is the possibility in some instances that the preservative may combine with certain constituents of the culture media, thus rendering part of it inert. This is known to be the case with such compounds as zinc chloride, copper sulfate and mercuric chloride. With the oils this objection probably does not enter so seriously, but even here it would be difficult to say what might occur in such heterogeneous compounds as the various tar distillates and similar substances of highly complex constitution.

Another variable which only a large number of tests can correlate is the difference in susceptibility among different fungi. Since molds are, as a rule, much more resistant to toxic agents than true wood-destroyers, the writers have avoided their use, as well as that of bacteria and yeasts. Even among the true wood-destroying fungi considerable variation exists,

TABLE I. LIST OF PRESERVATIVES TESTED SHOWING ESSENTIAL PROPERTIES AND KILLING POINT (a)

Preservative	Specific gravity 60° C.	Per cent distills below						Killing point (per cent)		Description	Coöperator	
		180° C.	215° C.	245° C.	275° C.	305° C.	320° C.	360° C.	Fomes annosus pinicola			
Wood tar (hardwood), No. 1561.....	1.195	About 27	About 31	51	..	..	..	..	1 25	0.75	Black viscous liquid with pyroigneous odor; 24 per cent water	Marden, Orth and Hastings, Chicago, Ill.
Wood creosote (Douglas fir), No. 1099.....	1.052	About 16	About 31	54.7	..	..	..	..	0.65*	0.20*	Black liquid with strong pyroigneous odor	Logged off Land Utilization Co., Seattle, Wash.
Spiritine wood preserver, No. 1932.....	1.006	14.2	23.2	35.2	36.7	..	..	..	Between 1 and 2	...	Reddish brown liquid; 0.47 per cent acid; a softwood creosote	Spiritine Chemical Co., Wilmington, N. C.
Water gas tar creosote, No. 1101.....	1.058	About 7	About 16	..	16.3	..	About 22	56.4	40+	40+	Mobile oily liquid with kerosene odor	United Gas Improvement Co., Philadelphia, Pa.
Water gas tar creosote, No. 2233 ..	1.042	3	6.7	21.2	35.3	48.5	53.7	77.6	Between 3 and 4	..	Dark brown liquid	United Gas Improvement Co., Philadelphia, Pa.
Water gas tar creosote, No. 2235 ..	0.995	3.3	12.8	37.7	61.7	75.3	80.3	..	Around 0.45	..	Greenish brown liquid	United Gas Improvement Co., Philadelphia, Pa.
Coal tar creosote, No. 1074 ..	1.048	4.8	17.8	44.4	54.1	67.2	74.1	..	0.55	0.225	Liquid, 8.4 per cent water	Creosote Supply Co., Chalmette, La.
Coal tar creosote, Fraction I, No. 1094 ..	0.934	35.1	78.3	..	..	..	..	..	0.30	0.225	Light liquid at room temperature	Smet-Solway Co., Ensley, Ala.
Coal tar creosote, Fraction II, No. 1106 ..	1.003	2 to 3	30	80	9.2	..	..	..	0.275	0.15	Naphthalene odor; nearly solid at room temperature	Smet-Solway Co., Ensley, Ala.
Coal tar creosote, Fraction III, No. 1107 ..	1.045	..	0.9	16.2	49.2	77.7	85	..	0.325*	0.125	Liquid at room temperature	Smet-Solway Co., Ensley, Ala.
Coal tar creosote, Fraction IV, No. 1108 ..	1.088	..	0.9	4.7	38.5	54.3	..	..	3.30*	0.125*	Liquid at room temperature	Smet-Solway Co., Ensley, Ala.
Coal tar creosote, Fraction V, No. 1109 ..	1.150	..	..	..	4.1	10.1	48.7	..	33*	7.80*	Heavy tarry liquid	Smet-Solway Co., Ensley, Ala.
Avenarius Carbolineum, No. 1843, ..	1.126	..	1.1	2.6	6.1	16.4	29	..	5.25	0.30	Thick liquid at room temperature; 191 per cent tar acids	Carbolineum Wood Preserving Co., Milwaukee, Wis.
S. P. F. Carbolineum, No. 1844 ..	(16°)	..	Below 10°	9	..	..	About 30	..	2.25	..	Thick dark brown liquid, 2.42 per cent tar acids	Bruno-Grosche and Co., New York City
C. A. Wood preserver, No. 1931 ..	1.120	0.5	2	4	8.2	20.6	28.9	70.1	Between 1 and 1.5	..	Brown liquid, probably high fractions of coal tar creosote	C. A. Wood Preserver Co., St. Louis, Mo.
Holzölter, No. 995 ..	1.113	7.3	7.8	9.9	12.8	23.8	29.6	58.9	Above 2.5	..	Thick, greenish brown liquid, partial emulsion ZnCl <sub>2</sub> and creosote oil with small amount of copper	Vanham Paint Co., Cleveland, Ohio
Copperized oil, No. 1098 ..	0.957	Below 10°	..	..	..	..	..	..	35*	40	Probably a crude petroleum with a little copper and vegetable oil to make a homogeneous solution	Ellis-Foster Co., New York City
End oil, No. 1103 ..	0.871	..	..	..	..	..	..	..	Above 6	..	Light liquid, odor of crude oil	F. W. Peters, Peabody Arsenal, Dover, N. J.
Kerosene, No. 1847 ..	0.798	25.1	65.5	89.7	..	..	..	..	Above 34	..	Refined petroleum oil	Standard Oil Co.
Cross sodium, No. 2086 ..	..	..	..	..	..	..	..	..	Between 0.14 and 0.28	..	Black, Wanch and Co., London, Eng.	..
Sonm-Such Spread, No. 2666 ..	..	..	..	..	..	..	..	..	Above 40	..	Yellow oily liquid with strong acrid odor; paint odor; chemical composition not known	George M. Stums, Trenton, N. J.
Sapwood antiseptic, No. 1611 ..	1.037	..	..	..	..	..	..	..	Above 75	..	NaCl, 2.92 per cent; CaSO <sub>4</sub> , 54.10; 0.182 per cent; CuSO <sub>4</sub> , 0.44; per cent; FeSO <sub>4</sub> , 4.11; 0.0695 per cent; ZnSO <sub>4</sub> , 7.14; 0.240 per cent (by weight)	J. W. Long, Chicago Ill.
Sodium fluoride, No. 1939 ..	..	..	..	..	..	..	..	..	0.25	0.15	Commercial salt meeting specifications	Cresswell Chemical Co., Cleveland, Ohio
Zinc chloride, No. 2239 ..	..	..	..	..	..	..	..	..	0.50	0.75	American Railway Engineering and Maintenance of Way Association	..
Zinc sulfide, No. 1711 ..	..	..	..	..	..	..	..	..	Above 30	..	Commercial salt	..

Zinc sulfide, No. 1711 ..

(a) In using these tables it should be noted that the figures given are checked to within an accuracy of 10 per cent. In the figures marked with an asterisk (\*) the killing point has not yet been checked in duplicate, in certain cases the killing point is given as "above" these figures, these figures indicate "around" certain killing points, and the figures are close to the true value but may be considerably higher or lower. The figures indicated as "above" a certain concentration, the result merely indicates that this is the highest concentration yet tested and the ultimate killing point may be considerably higher.



as will be seen in the tables following, but this is usually within narrower limits.

Both the fungi used by the writers grow well on the media employed, *Fomes annosus* Fr. covering the surface of the petri dish in about 20 days and *Fomes pinicola* (Sw.) Fr. in about 15.

Table I shows a list of the preservatives tested, together with salient properties, and the concentration necessary to prevent growth of the organisms. In this table the preservatives have been grouped according to their nature, such as coal tar, water gas tar, and wood tar distillation products, petroleum oils and water-soluble inorganic salts, in order to give an easy direct comparison.

In general the table shows that the two fungi react, in most cases, quite differently to the same substance, *Fomes pinicola*, as a rule, being a far less resistant organism than *Fomes annosus*. With *Fomes annosus* the first three fractions of coal tar creosote are consider-

properties and the 0.995 oil proving at least, or more, toxic than coal tar creosote.

Petroleum oils, according to the three samples tested, have low antiseptic value.

Cresol-calcium in these tests shows a high toxicity and the poor results reported against it in practice are apparently due to a change in chemical constitution which did not take place under our method of testing.

Zinc chloride, in the commercial form, is slightly more toxic to *Fomes annosus*, and far less toxic to *Fomes pinicola*, than coal tar creosote.

Sodium fluoride is over twice as toxic to *Fomes annosus*, and about one and one-half times as toxic to *Fomes pinicola*, as coal tar creosote.

While the work has not progressed far enough with zinc sulfate to give conclusive results, the indications are that it compares very favorably with both zinc chloride and coal tar creosote.

TABLE II PRESERVATIVES ARRANGED IN ORDER OF TOXICITY AND SHOWING RATIO TO COAL TAR CREOSOTE  
Killing point

Preservative	Per cent	Fomes annosus				Fomes pinicola			
		Lbs. cu. ft.		Ratio to coal tar creosote No. 1074		Lbs. cu. ft.		Per cent	
Coal tar creosote, Fraction II, No. 1106.....	0.225	0.140	2.5	1.5	0.094	0.15			
Sodium fluoride, No. 1929.....	0.25	0.156	2.2	1.5	0.094	0.15			
Cresol-calcium, No. 2098.....	0.14-0.28	0.087-0.174	3.9-2.0						
Coal tar creosote, Fraction I, No. 1094.....	0.30	0.187	1.8	1.0	0.140	0.225			
Coal tar creosote, Fraction III, No. 1107.....	0.325*	0.203	1.7	1.8	0.078	0.125			
Water gas tar creosote, sp. gr. 0.995, No. 2235.....	Around 0.45								
Zinc chloride, No. 2239.....	0.50	0.312	1.1	0.3	0.468	0.75			
Zinc sulfate, No. 1711.....	Around 0.50								
Coal tar creosote, No. 1074.....	0.55	0.343			0.140	0.225			
Wood creosote, No. 1099.....	0.65*	0.405	0.84	1.12	0.125	0.20*			
Wood tar, No. 1561.....	1.25	0.78	0.44	0.3	0.468	0.75			
C. A. Wood preserver, No. 1931.....	1-1.5	0.6-0.9	0.55-0.37						
Spiritine wood preserver, No. 1932.....	1-2	0.6-1.2	0.55-0.27						
S. P. F. Carbolineum, No. 1844.....	2.25	1.404	0.24						
Holzhefner, No. 2097.....	Above 2.5								
Coal tar creosote, Fraction IV, No. 1108.....	3.3*	2.059	0.16	1.8	0.078	0.125*			
Water gas tar creosote, sp. gr. 1.042, No. 2233.....	3-4	1.9-2.5	0.18-0.14						
Avenarius Carbolineum, No. 1843.....	5.25	3.27	0.104	0.75	0.187	0.30			
Fuel oil, No. 1103.....	Above 6								
Kerosene, No. 1847.....	Above 34								
Coal tar creosote, Fraction V, No. 1109.....	33*	20.59	0.017	0.029	4.867	7.80*			
Copperized oil, No. 1095.....	40	24.96	0.015	0.0056	25+	Above 40			
N. S. Special, No. 2696.....	Above 45	28+	0.014-	0.0045	31.2+	Above 50			
Water gas tar creosote, sp. gr. 1.058, No. 1101.....	Above 40	25+	0.016-	0.0056	25+	Above 40			
Sapwood antiseptic, No. 1611.....	Above 75	46.8+	0.007-						

ably more toxic, and the last two fractions much less toxic, than the oil itself; with *Fomes pinicola* only the last fraction is less toxic. This indicates the advantage, from a toxicity standpoint, of removing at least a part of the heavier tar oils.

The carbolineums and similar products which consist, in the main, of the higher boiling constituents of creosote in all cases proved much less toxic than coal tar creosote.

Wood creosote from Douglas fir appears to compare very favorably with coal tar creosote, but the softwood creosote, under the trade name of Spiritine Wood Preserver, which has a much lower specific gravity, appears to be much less effective.

In the case of water gas tar creosotes the toxicity increased rapidly with decreasing specific gravity, the heavier 1.058 oil possessing very low antiseptic

None Such Special, which is claimed by the manufacturers to water-proof and give a hard finish to timber, as well as to prevent or stop decay, proved very low in toxic properties, and even stimulated growth in high concentrations; however, the physical properties, when injected into wood, may be such as to exclude fungus growth and thus substantiate the claims made for it.

In Table II the preservatives are arranged in the order of their toxicity to *Fomes annosus*, the concentrations are reduced to pounds per cubic foot and the ratios of their efficiency as compared with coal tar creosote are presented. Had the preservatives been listed in their order of toxicity to *Fomes pinicola* the arrangement would have been somewhat different and Avenarius Carbolineum and creosote Fraction IV would have appeared higher in the scale, and creosote Fraction I and zinc chloride considerably lower.

It is seen that ten of the twenty-five preservatives tested fall below 1 per cent, or more accurately 0.65 per cent, for their killing point for *Fomes annosus*; *Fomes pinicola* was used with only fourteen of them but of these ten fell below 1 per cent, or more accurately, 0.75 per cent.

It is interesting to note that sodium fluoride and Fraction II of coal tar creosote head the list with nearly equal toxicities. Just what constituents of the naphthalene fraction are the effective ones is not known at present, but the work of other investigators indicates that pure naphthalene has low toxic properties. The very favorable results from sodium fluoride would place this in the first rank of water-soluble preservatives. This, together with several other fluorine compounds, has come into considerable use abroad, particularly in Austria, and it is the opinion of the writers that we have in these substances very efficient wood preservatives which can be adapted to use in many situations. The industry particularly needs some substance which can safely be recommended for building timbers.

In comparing the two carbolineums with coal tar creosote it is seen that approximately 30 per cent of the former distills below 320° C., while 74 per cent of the creosote comes over. This indicates the greater toxicity of the lower boiling constituents. As to what causes the greater toxicity of S. P. F. Carbolineum over Avenarius Carbolineum we are not prepared to say, but the fact that the former is higher in tar acids is very suggestive.

The poor showing made by copperized oil against both fungi indicates that adding copper in this form to low-toxic petroleum or vegetable oils is of very doubtful value.

In conclusion, the writers are prone to take a very conservative position when it comes to analysis of the data presented and generalizations drawn therefrom. We wish to strongly emphasize again the fact that toxicity alone does not necessarily give a direct comparison of the service value of preservatives, and that all the statements made comparing different substances refer to the toxic properties only. However, we do feel that the results here set forth will prove of considerable value in outlining further tests which will serve to bring out actual service values.

We wish to record our acknowledgments to Dr. Haven Metcalf, Pathologist in Charge, Laboratory of Forest Pathology, Bureau of Plant Industry, Washington, D. C.; to Mr. Howard F. Weiss, Director of the Forest Products Laboratory, U. S. Forest Service, Madison, Wisconsin, for facilities and material placed at our disposal; also to Mr. Ernest Bateman, Chemist in Forest Products, Forest Products Laboratory, who has supplied all the data on the physical and chemical properties of the preservatives examined.

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#### A RAPID METHOD FOR DETERMINING THE PERCENTAGE OF CASEIN IN MILK

By W. O. WALKER

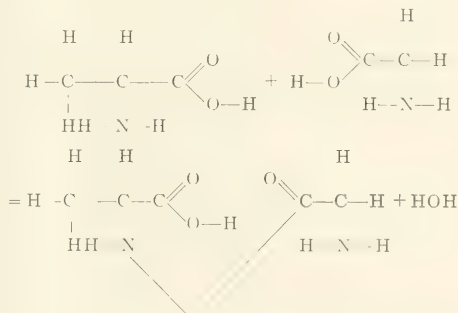
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During the past few years dairymen have been

giving a good deal of attention to the advisability of taking into account the percentage of casein when paying patrons for milk to be used in cheese-making. Some advocate paying on a fat basis only, others on the fat and casein basis. It is not the object of this article to discuss the merits of either of these methods, but to outline a process which has been tried out in the author's laboratory for quickly and simply arriving at the amount of casein in milk.

It is well known that several methods have been suggested of late, the most promising probably being the centrifugal method of Hart. This has, apparently, yielded satisfactory results in many cases, but has been found to give varying results with preserved samples, and with fresh milk, under different conditions of temperature, etc.

Research into the constitution of the protein molecule has revealed the probability of its consisting of a complex linkage of a large number of amino acids. To illustrate this linking up of amino acids we may use the following equation, which shows how one molecule of a simple amino acid, such as amino-propionic acid, may become bound to a molecule of another amino acid such as amino-acetic acid:



Both the molecules of amino-propionic acid and amino-acetic acid, as indicated above, possess an

alkaline (amino) group,  $\text{H}-\text{N}-\text{H}$ , as well as an acidic

group,  $\text{C} \begin{smallmatrix} \text{O} \\ // \\ \text{OH} \end{smallmatrix}$ , and when they combine we may

have the union taking place in the manner indicated, in which the alkaline (amino) group of one molecule interacts with the acidic group of the other molecule, thus leaving an alkaline group and an acidic group still existing in the product, which may be looked upon, for our purpose, as a very simple representative of the proteins.

It has further been observed that when formaldehyde is added to proteins, the neutral character of the molecule disappears, with the result that the acidic property predominates strongly. It is thought that the formaldehyde reacts with the alkaline groups forming methylene derivatives, thus leaving the acidic groups free to act. These acidic groups may now be neutralized with standard alkali, and if the value of the alkali in terms of protein be known, the percentage of protein present may be estimated.

Hugo Schiff<sup>1</sup> was the first to point out the importance of the reaction between formaldehyde and amino acids. S. P. L. Sorensen worked out most of the details for the quantitative application of the reaction for estimating amino acids. H. Droop Richmond adapted the reaction to the estimation of total proteins in milk.

The author decided to apply the reaction to the estimation of casein in milk, with the use of the alkali commonly used for the 'acid test' now in general use in cheese factories in Ontario.

In hoping to apply the reaction to estimate casein only, the problem is, of course, to obtain the proper factor, which, when multiplied by the quantity of alkali necessary to neutralize the acidity developed after treatment with formaldehyde, will give the quantity of casein in the sample. Since the formaldehyde reacts with both casein and albumin, and, since the amounts of these two in milk do not bear a constant ratio to one another, it was not to be expected that a factor holding good in all cases could be obtained. However, a factor has been obtained that is giving unexpectedly good results.

The alkali solution was ninth normal sodium hydroxide, and the formaldehyde was the commercial article (40 per cent) made neutral to phenolphthalein.

The method for arriving at the factor was the following: 10 cc. of milk were transferred by means of a pipette to a porcelain casserole. A fairly large quantity of phenolphthalein solution (about 1 cc. of a 1 per cent solution) was added next. The alkali was then run in with constant stirring with a glass rod until a fairly deep pink color developed. So far the test is exactly the same as the ordinary "acid test." No account was kept of the alkali used to bring the sample of milk to the neutral point. About 2 cc. of the neutral formaldehyde solution were next added, with the result that the pink color at once disappeared. The reading of the burette was then taken, and alkali again added with stirring until the same degree of color developed. The reading of the burette was again taken, the difference between the two readings being the amount of alkali used in the second titration.

In determining the percentage of casein in a given sample of milk the procedure is exactly as outlined for determining the factor, omitting the Kjeldahl determination. The test occupies only a few moments. It has, of course, the disadvantage that only one sample can be handled at a time, but as a number of samples can be run in a few minutes, this may not prove to be of very great consequence.

From the fact that the chemicals and apparatus required are exactly the same as are in common use in cheese factories, with the exception of the formaldehyde which is very inexpensive, it is thought that the method should commend itself to the serious consideration of dairymen. It is, of course, important that the formaldehyde solution be kept neutral. This may be accomplished by adding a few drops of the indicator solution (phenolphthalein) to the formaldehyde in the bottle, and then adding the alkali until a pink color develops. This fades in the course of time, and the formaldehyde must then be treated again with the alkali.

The proper amounts of indicator (1 per cent solution) and formaldehyde solutions to be used have been found to be about 1 cc. of the former and 2 cc. of the latter. An excess of either, however, occasions no error. In the manipulation of the test it is well to add sufficient of the alkali during the first titration to bring the color to a decidedly deep pink, and at the second titration to bring the color to the same shade. The titrations are best carried out in a white cup or porcelain casserole.

If it is desired to estimate the acidity also, the reading of the burette may be taken after the first titration.

The casein is then estimated from the difference between the first and second titrations. Thus both the acidity and the casein are estimated in the one operation. Those dairymen who use *N*/10 alkali and 9 cc. of milk as the sample will, of course, employ the same factor. The test is at present recommended for unpreserved milk only, although the author expects to be able to announce a suitable preservative at an early date.

The following table is given for the use of those not wishing to take the time to multiply the amount of alkali used by the factor 1.63.

Sample	Kjeldahl method	New method	Difference
1.....	2.45	2.53	+0.08
2.....	2.45	2.45	0.00
3.....	2.61	2.63	+0.02
4.....	2.51	2.52	+0.01
5.....	2.57	2.60	+0.03
6.....	2.53	2.61	+0.08
7.....	2.32	2.36	+0.04
8.....	2.96	2.96	0.00
9.....	2.69	2.66	-0.03
10.....	2.48	2.46	-0.02
11.....	2.32	2.30	-0.02
12.....	2.52	2.56	+0.04
13.....	2.31	2.27	-0.04

Another 10 cc. of milk was next treated by the official Kjeldahl method for casein, and from this result the value of 1 cc. of *N*/9 alkali in terms of casein was determined. From a large number of samples the value: 1 cc. *N*/9 alkali = 1.63 per cent casein was arrived at. Above is a comparison of some results obtained by the official Kjeldahl method and the new method, using the factor 1.63.

Cc. <i>N</i> /9 alkali used	Per cent casein
1.00.....	1.63
1.05.....	1.71
1.10.....	1.79
1.15.....	1.87
1.20.....	1.95
1.25.....	2.04
1.30.....	2.12
1.35.....	2.20
1.40.....	2.28
1.45.....	2.36
1.50.....	2.44
1.55.....	2.53
1.60.....	2.61
1.65.....	2.69
1.70.....	2.77
1.75.....	2.85
1.80.....	2.93
1.85.....	3.01
1.90.....	3.10
1.95.....	3.18
2.00.....	3.26

Instead of using a 10 cc. pipette for taking the

<sup>1</sup> *Analyst*, **310**, 28 (1900); **319**, 89 (1901); **325**, 48 (1902).



samples and consequently having to multiply the amount of alkali used by 1.63, it is advisable to use a 16.3 cc. pipette, in which case, the reading on the burette denotes directly the percentage of casein.

A very convenient and simple form of acidimeter has been lately put on the market by the author which may be used for both the "acid test" and the "casein test."

A series of comparative tests, using both the new method and the centrifugal method, has been carried on at the Eastern Dairy School, Kingston. The tests were made independently on the same milks by Messrs. Echlin and Cameron. Mr. Echlin did the work with the new test, and Mr. Cameron that with the centrifugal method. The resulting figures, as can be seen from the following table, are in surprisingly close agreement.

Centrifugal method	New method	Centrifugal method	New method	Centrifugal method	New method
2.6	2.64	2.25	2.35	2.2	2.27
2.7	2.69	2.3	2.35	2.4	2.43
2.5	2.44	2.35	2.43	2.4	2.43
2.55	2.61	2.6	2.59	2.4	2.43
2.55	2.61	2.5	2.51	2.5	2.59
2.55	2.61	2.5	2.51	2.45	2.51
2.3	2.36	2.25	2.27	2.4	2.43
2.3	2.36	2.25	2.27	2.4	2.43
2.6	2.61	2.2	2.19	2.45	2.49
2.5	2.53	2.35	2.35	2.5	2.55
2.5	2.53	2.35	2.35	2.3	2.27
2.25	2.28	2.35	2.35	2.35	2.35
2.25	2.28	2.4	2.43	2.4	2.43
2.2	2.20	2.4	2.43	..	..
2.5	2.56	2.35	2.35	..	..
2.6	2.63	2.35	2.35	..	..
2.7	2.67	2.35	2.35	..	..
2.3	2.43	2.3	2.27	..	..
2.3	2.43	2.3	2.27	..	..
2.5	2.43	2.4	2.43	..	..
2.45	2.35	2.4	2.43	..	..
2.56	2.67	2.4	2.43	..	..
2.56	2.67	2.3	2.27	..	..
2.55	2.59	2.25	2.27	..	..
2.55	2.59	..	..	..	..
2.55	2.59	..	..	..	..

The average difference for the above sixty-three determinations is 0.03+.

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## I. A NEW ELECTRICALLY CONTROLLED AND TIMED ASPHALT PENETROMETER

## II. THE EFFECT ON PENETRATIONS OF VARIATIONS IN STANDARD NEEDLES

By HERMANN W. MAHR  
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### I

Success in the laying of asphalt pavements is probably more dependent on the proper consistency of the asphalt cement used to bind the mineral aggregate than on any other feature. The varied origins of modern bituminous cements have made the determination of their consistency the most important test applied to these materials. Formerly a few varieties of standard solid bitumens, quite uniform in character, fluxed with definite proportions of petroleum residuums of standard and specified composition, yielding cements of a desired consistency, formed the bulk of the asphaltic cements; but recently many paving bitumens obtained by distilling asphaltic

petroleums to the consistency of cements have come on the market. Proximate chemical analysis is of little value in fixing their origin, and the highway chemist is obliged to rely almost solely on determinations of consistency to ascertain their suitability.

There are several rough methods for determining the consistency of asphaltic cements, but the most generally used scientific determination is by means of penetrometers. The first of these instruments was devised by Bowen, and has been followed by machines working on the same principle by Kenyon, Dow and the New York Testing Laboratory. The two latter are those generally used at present. The penetrometer has made it possible to control the consistency or as usually expressed, the penetration, within narrow limits.

The penetrometers consist essentially of a needle of specified size (Roberts, No. 2) fixed in a rod, the rod and needle being of, or loaded to, definite weights. A clamp of some nature holds the rod with the needle, allowing the latter to penetrate as nearly as possible without friction. A device for measuring the amount the needle has penetrated after it has been released for a specified time and again grasped by the clutch, is also necessary. The penetration is expressed in hundredths of a centimeter.

Penetrations are most commonly made at 25° C. (77° F.) with the needle loaded to 100 grams penetrating for five seconds. In order to ascertain the extent an asphaltic cement will harden when chilled to 0° C. (32° F.), penetrations are frequently made at this temperature with the needle loaded to 200 grams penetrating for one minute. Occasionally it is specified that cements shall not show more than a stated penetration at 37.7° C. (100° F.) or 46° C. (115° F.), the needle being under a weight of 50 grams and released for five seconds.

The Dow penetrometer frame consists of a base to which is fastened a broad upright support with two shelves at different distances from the base. The needle is held in an aluminum rod weighted by a rectangular frame of the same metal. The latter is fixed to the rod at about one-third the distance from its lower end. Weights are placed on the lower part of the frame to load the needle. The above-mentioned framework encloses the lower shelf on which is placed the sample. The rod passes through a hole in the upper shelf and is here grasped by the clamp which is closed on the rod by a spring when not penetrating. The rod and needle are released from the clamp by pressing the spring together with a button-ended rod.

The device for measuring the amount penetrated is fixed above the end of the rod. This consists of a rack, set vertically, the end of which can be brought down to meet the top of the rod. This rack is in gear with a pinion on a horizontal shaft. The latter passes through a graduated dial and an adjustable hand is fastened to it there. A counterweight which hangs from a cord winding up on a small pulley on the pinion shaft allows the rack to be raised or lowered. The divisions on the dial correspond to a movement of 1/100 cm. by the rack.

The Dow instrument has many features which make its use time-consuming. It also requires considerable skill and attention to obtain results checking within three or four degrees. The shelf, on which rests the water bath containing the sample, is fixed in position. This limits the height of the sample container and the bath. The weighted frame limits the width of the vessel used for a water bath, and is an inconvenience in placing the sample on the shelf and setting the needle. When the clamp is opened the space within is quite large. This allows the rod to deviate from a vertical position while penetrating. The weight of the large frame also tends to bring the needle out of the vertical. To avoid this action requires extreme care in setting, and even then it takes place to a small extent. When the rod is again clasped by the clamp, it is moved horizontally, thus bringing a force on the needle other than its weight. On bringing the rack down on the rod, after the needle has been set or penetrated, its weight is liable to drive the rod and needle down into the asphalt. The operator is inclined to avoid this by stopping the rack just above the top of the rod, thus introducing inaccuracies in the determination. The counterweight and its cord often become tangled in the shaft and shelves and are in the way.

These objectionable features of the Dow penetrometer led the New York Testing Laboratory to modify it. This instrument is described by Clifford Richardson in his work on asphalt paving.<sup>1</sup> The fixed shelf of the Dow machine is replaced by one on a screw. This allows the sample to be brought up to the needle very slowly, and the setting can be made with greater accuracy. The weighted frame is dispensed with and replaced by a weight on the lower part of the rod just above the needle. The rod slides in a collar of considerable height and is thus maintained in a vertical position. The clamp holding the rod is fixed in this collar and grasps it more firmly than that of the Dow penetrometer. Instead of a counterweight, the rack is kept in position by a spring pressing against it.

The wide collar, forming part of the clamp of the New York Testing Laboratory instrument, gives rise to considerable friction on the rod. This violates the basic requirement of the ideal penetrometer. The clamp requires the exertion of considerable force to release the rod. This tends to cause the operator to allow the clamp to shut before the expiration of the standard penetrating period. The force required to open the clamp is also liable to disturb the setting of the instrument and thus introduce inaccuracies.

The errors due to the construction of the present machines and to the personal equation of the operator often require a long series of determinations in order to obtain three results which lie within a limit of three or four degrees. Some specifications for asphaltic cement require its consistency to lie within limits ten degrees apart on the penetrometer. It is therefore difficult to interpret the specifications strictly with the results obtained on the present penetrometers. This has given rise to a demand for an instrument which eliminates some of the constructional errors of the present ones, and also some of the personal errors.

The errors in penetrating, apart from those of the instrument, are quite numerous. The sample, usually contained in a small tin box, must be firmly set in the water bath. This can be very satisfactorily accomplished by means of a glass vessel with a deep layer of fairly hard asphaltic cement.<sup>1</sup> The sample must have been at the standard temperature long enough to have attained it throughout. In this connection, laboratories working with a large number of asphaltic cements will find a good thermostat a great convenience. After a sample has been maintained thirty minutes at constant temperature it can be placed in the penetrometer water bath, filled with water from the thermostat at the same time.

A personal error of considerable magnitude has already been indicated, that of setting the rack on the rod before and after penetrating. In the timing of the penetration period lies probably the greatest error of the determination. The timing is done by either a stop-watch or a metronome. The use of the former is more open to inaccuracies than the latter.

The variation in the size of the standard needles has often been pointed out as a source of variation in results obtained by different chemists or by the same operator from time to time. The personal errors have been so large that no definite conclusions could be drawn as to the extent of this source of difference.

The importance of eliminating the time error and shock, due to the manual control of penetrometers, has long been recognized. With this object in view, Dow and Griffith devised and patented<sup>2</sup> an electrical limiting-time-interval clamp, to be applied to the then generally used Bowen penetrometer. This clamp clasped the thread supporting the weighted bar which held the needle, and released it for the desired intervals. This electrical limiting-time-interval clamp was cumbersome and complicated in its working and regulation. When Dow devised the penetrometer which bears his name, and which superseded the Bowen instrument, he omitted from it his time-interval clamp.

The advent of the simple, compact, Sieman's intermediate relay with time limits has made it possible to electrically time and control penetrometers of the present type. The penetrating device of the instrument can be directly controlled by the electrically timed magnet, instead of through the intermediary of a clamp, as in the Bowen-Dow-Griffiths electrical penetrometer. This simplifies the operating mechanism and reduces the chances of trouble from its derangement.

A new form of penetrometer, electrically controlled and timed, used for over a year in this Laboratory, is shown in Figure 1. Figure 2 is a sketch of the electromagnetic clutch for holding the rod with its needle. The clutch is on a bracket sliding on the upright rod of the instrument, to which it may be secured by means of a set screw. The weighted rod A, which holds the needle, is of steel, brass-clad. It slides through the openings in the thin German silver plates, C C, and is partly enclosed by the concave poles, B, B<sub>2</sub>, of the electromagnet. The plates are set so the rod does not come into contact with the poles of the magnet, and are

<sup>1</sup> "The Modern Asphalt Pavement," John Wiley & Sons

<sup>1</sup> Bull. 38, Office of Public Roads, U. S. Dept. of Agriculture.

<sup>2</sup> U. S. Patent 512,687 (1894).

rounded where they touch the rod, thus eliminating all friction. The rod and needle weigh 50 grams and are weighted to 100 and 200 grams by weights of 50 and 150 grams, respectively, slipped over the rod above the needle, and there fastened by set screws.

The penetration is measured, as in other machines, by means of a rack and pinion, the latter being fastened to an adjustable hand on a dial. The counterweight and spring, used in the previous types of instruments for holding the rack in place, are dispensed with. The pinion shaft has an additional gear wheel. This gear is in mesh with a worm on a shaft at right angles to the first, the worm shaft being driven by means of a milled head at one side of the dial. By turning the milled head the rack may be raised or lowered and accurately set on top of the rod. In setting the needle on the surface of the sample, the latter is first raised to within less than a millimeter of the former. The rod is then forced down by the rack until the needle touches the surface of the asphaltic cement. During the setting the rod is held by the magnet, the electro-magnetic force being overcome by that exerted by the

operated by hand. The circuit is broken by pressing a button. To eliminate the time error of the observer, a Sieman's intermediate relay with time-limit is used. The penetrometer is placed in the circuit with one side of this device, and the lighting circuit passed through a switch and the relay electro-magnet. On breaking the current through the latter, the penetrometer circuit is broken and automatically made at the end of five seconds.

The accuracy of the penetrometer was tested by determining the penetration of three asphaltic cements, using the same needle. The penetrations were made at 77° F., with the needle loaded with 100 grams, penetrating for 5 seconds. After each observation the needle was cleaned with chloroform, dried, and brought to 77° F.

The results are given in the following table:

PENETRATION OF ASPHALTIC CEMENTS. (77° F., 100 g., 5 sec.)

	Oil asphalt cement No. 1	Oil asphalt cement No. 2	Trinidad asphalt cement
Determination No. 1.....	55	53	85
Determination No. 2.....	55	53	84
Determination No. 3.....	55	53	84

## II

Richardson<sup>1</sup> has stated that variations in the size of the needles give rise to uncontrollable variations in penetrations determined with them.

Since all errors are eliminated in the machine described, it was possible to ascertain the extent of this variation. Three needles were selected from each of three packages of standard needles. Oil asphalt cement No. 1 was then penetrated, using these needles, taking the precautions outlined above.

PENETRATION OF OIL ASPHALT CEMENT No. 1, BY DIFFERENT NEEDLES (77° F., 100 g., 5 sec.)

Needle	Package	Penetration	Needle	Package	Penetration
1	1	55	6	2	55
2	1	55	7	3	55
3	1	54	8	3	54
4	2	54	9	3	54
5	2	54			

Average, 54.6

The greatest deviation from the mean is 0.6 of a unit.

**CONCLUSIONS.**—A new form of penetrometer, which eliminates the errors due to the construction of previous instruments and permits rapid accurate determinations, has been described.

The personal error in timing penetrations has been eliminated through the use of this penetrometer in connection with an intermediate relay with time-limit.

The variations in determinations of penetration due

<sup>1</sup> Loc. cit.



Fig. 1

rack. This device and method of procedure enable very accurate settings of the needle and rack to be made.

The sample is placed on a movable shelf which can be rapidly lowered to allow cleaning of the needle. In order to set the machine in a vertical position, a plumb bob and adjusting screws are attached to the penetrometer. A small electric lamp, fastened to the top of the standard and in series with the electro-magnet, indicates when the current is on. The instrument is wound to be connected to a 110 volt direct current circuit.

The use of the electro-magnet clutch precludes the shock or displacement of the machine, due to a clamp



to variations in the standard needles has been investigated and found to be negligible.

The writer wishes to express his appreciation of the help rendered by Mr. Walter Erlenkotter and Mr. A. D. St. John, of this Laboratory, in connection with this paper.

STANDARD TESTING LABORATORY  
BOARD OF ESTIMATE AND APPORTIONMENT  
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## AN APPARATUS AND METHOD FOR DETERMINING THE HARDNESS OF BUTTERFAT

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The desirability of having an accurate method for determining the hardness or consistency of butterfat and other fats has been felt for a number of years. Several methods and apparatus having a greater or less degree of efficiency have been devised from time to time.

The first methods were proposed for the examination of olive oil. Of these earlier methods the most practical was devised by Serra Carpi.<sup>1</sup> His method was to cool the olive oil down to 20° C., for three hours, and by means of a suitable arrangement, he placed on the solidified fat a cylindrical iron rod, 2 mm. in diameter and 1 cm. long and conical at the bottom. Weights were then put on to the rod until it sank completely into the fat. Thus, for pure olive oil 1700 grams and for cottonseed oil 25 grams were required.

Woods and Parsons<sup>2</sup> report satisfactory results in determining the hardness of butter by the use of a method which consists essentially of dropping a weighted glass rod through a glass tube 1 meter long, held vertically above the surface of the butter to be tested, and noting the depth of penetration on a scale attached to the glass tubing. The determinations were performed at 15.5° C. after the butter had stood in a cool room for several days. The results were expressed in mm. of penetration.

R. Brulle<sup>3</sup> measured the hardness of butter with an apparatus which he called an "oleogrammeter." This is an instrument consisting of a vertical rod on the top of which is fixed a large plate. The rod is allowed to slide in a ring fastened to a stand. The end of the rod is placed on the surface of the solidified fat, and then weights are put on the dish until the rod sinks briskly into the fat. The weights required represent the resistance of the butter to the "oleogrammeter." The butter samples were kept at 21° C. for an hour before testing. This method is essentially the same as that used by Serra Carpi<sup>4</sup> for olive oil.

Sohn<sup>5</sup> proposes three forms of apparatus and lays down the following rules, strict adherence to which are necessary:

1. The rod must descend in an absolutely perpendicular direction.

2. It must slide in its bearing with the least possible friction.

3. Conditions of temperature must be constant.

4. Vessels of one diameter must be used for the material under examination.

5. The rod must enter the center of the vessel or at a fixed distance from the circumference.

6. The same depth of material must always be used.

7. The material must be allowed to rest a certain fixed time before testing.

J. B. Lindsey<sup>1</sup> and his associates determined the hardness of butter with an apparatus analogous to that used by Woods and Parsons,<sup>2</sup> the only real difference being that they dispensed with the large glass tube and the depth of penetration was measured on the plunger. Their determinations were performed on butter which had been in cold storage for some time and then allowed to stand at room temperature for several hours.

Hunziger, Mills and Spitzer<sup>3</sup> report results in measuring the hardness or "mechanical firmness" of butter with an apparatus which measured the crushing effect of a plunger, size and weight not stated, on briquettes of manufactured butter. No mention is made of the conditions of temperature under which the tests were conducted.

In some of our experimental work here, we considered it desirable to measure the hardness of butter fat with a reasonable degree of accuracy, and in such a way that results obtained throughout experiments extending over long periods of time would be entirely comparable. After trying several of the above-mentioned methods, none of which proved delicate enough for our purpose, the following apparatus and method were devised.

The apparatus used, as shown in the accompanying cut, comprises a firm support (A) and a separate light frame (B) carrying the penetrating needles and the weights. The support consists of a heavy iron base (c) into which are inserted 2 upright rods (d and e) about 1 meter long, one of which is hollow and contains wires connecting the electro-magnet (g) with (h). These uprights are about 25 cm. apart and are joined together at the top by a piece of hollow iron rod (f); (h) and (i) are binding posts for attaching the batteries to operate the magnet. A key (j) attached to the base serves for making and breaking the current through the magnet; (k) and (l) are millimeter scales reading downward. Attached to the upright rods is an adjustable platform (m) for carrying the sample whose hardness is to be tested. The coarser adjustment of the height of the platform is secured by means of the clamps (n) and (o). This adjustment does not need to be regulated except at rare intervals. A finer adjustment is secured by simply turning (m) which is supported from (n-o) by a 3/4 inch nut and screw. The frame is of hollow brass tubing to get it as light as possible, while still retain-

<sup>1</sup> Serra Carpi, *Z. anal. Chem.*, 1884, **23**, 566.

<sup>2</sup> Woods and Parsons, *Rev.* 13 New Hampshire Eng. Sta.

<sup>3</sup> R. Brulle, *Compt. rend.*, 1893, **116**, 1255.

<sup>4</sup> *Loc. cit.*

<sup>5</sup> Sohn, *Analyst*, 1893, p. 218.

<sup>1</sup> Lindsey and Associates, 13th Ann. Rept. Hatch Exp. Sta., p. 28;

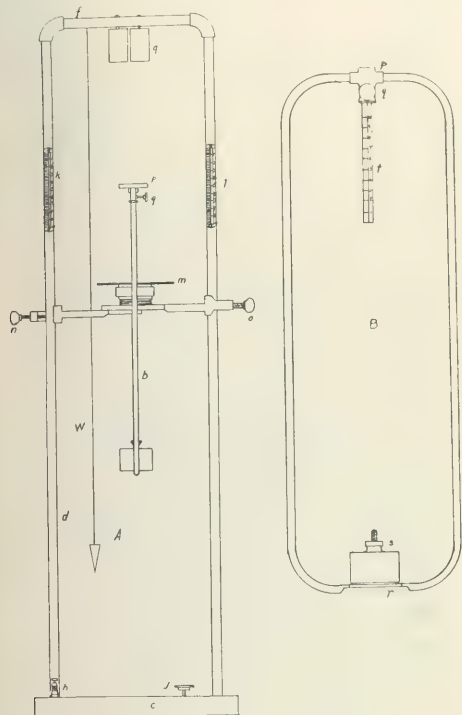
14th Ann. Rept. Hatch Exp. Sta., p. 29; 16th Ann. Rept. Hatch Exp. Sta., p. 54.

<sup>2</sup> 15th Ann. Rept. Hatch Exp. Sta., p. 99.

<sup>3</sup> Woods and Parsons, *loc. cit.*

<sup>4</sup> Bull. 169, Purdue University, Indiana Agr. Exp. Sta.

ing the necessary degree of strength. It is about 40 cm. long and 15 cm. wide: (*p*) is a piece of soft Swedish iron to be acted on by the magnet. Directly beneath this inside the frame is a socket and a set-screw (*q*) to hold the needle (*l*) in place. At the opposite end of the frame is a small platform (*r*) for



carrying the weights, which are made with a hole drilled through the center so that they can be placed over the screw projecting above the platform and held firmly in place by the nut (*s*). The frame (*B*) when carrying any one of the set of needles weighs 200 grams. Additional weights are provided, making possible any combination of exact multiples of 100 grams up to 1400. A set of needles is provided having cross-sectional areas of 5, 10, 15, 25, 50 and 100 sq. mm. They are cylindrical in shape and slightly more than 10 cm. long, being marked at a distance of 10 cm. from the end. The larger sizes are of hollow tubing plugged at the ends, and the smaller made with heavy shanks to secure uniformity of weight. The scales (*k* and *l*) attached to the upright rods which were previously referred to, are so placed that when the frame with needles and weights is held in place by the electro-magnet, preparatory to making the test, the point of the needle is at zero on the scales. The height of the adjustable platform (*m*) is then so regulated that the surface of the sample to be tested is at 100 mm. on the scale. A small plumb bob (*W*) or a wooden rod of proper length measuring downward from (*g*) is made use of

in this connection. The distance of fall before reaching the surface of the butter is, then, always 10 cm.

In making the determination, the frame (*B*) with a suitable needle and weights is suspended from the electro-magnet, and the beaker of fat placed in position beneath the needle, the height being regulated as described above. The frame is then released by means of the key. The depth of penetration is ascertained by stretching a very fine wire in line with the mark on the needle, and noting its position on either scale. The average of the two readings is taken as the depth of penetration. Since the cross-sectional area of the penetrating needle is known, and the depth of penetration has been ascertained, their product indicates the volume of butterfat displaced. The amount of weight acting on the needle is known, and the distance through which it falls is constant; if then, the amount of weight employed, expressed in grams, is divided by the volume of fat displaced, expressed as cu. mm., the quotient will represent the weight in grams required to displace 1 cu. mm. of the fat, or the number of kilos required to displace 1 cc. at the stated temperature. This is the basis employed to express the proportionate hardness of the fat. A sample of fat is said to have a hardness of 1 at a given temperature when 1 kilo will displace 1 cc. of fat; or of 1.2 or 0.85 when 1200 or 850 grams, respectively, are required to displace 1 cc. of fat. When all other conditions are constant, it is evident that the hardness is in inverse proportion to the depth of penetration, and direct comparisons can be made.

The amount of weight employed and the size of the needle used will depend, of course, on the character of the fat, and the temperature at which the hardness is determined. With a proper combination of needles and weights, the needle will remain practically stationary in the fat after the initial plunge. If, however, too much weight or too small a needle is employed, the needle continues to sink slowly, making an accurate reading of the depth of penetration impossible. In the reverse case with too large a needle or too little weight, the penetration is of course much less, and the percentage experimental error proportionately greater.

The suspension of the weights far below the needle brings the center of gravity of the falling portion of the apparatus below the point of the needle, causing the latter to invariably assume a vertical position, making it much easier to ascertain the true depth of penetration than would be the case if the point of the needle (*l*) were at or below the center of gravity. After its release by the electro-magnet, the apparatus meets with no resistance whatever in its fall, except that offered by the air until the point of the needle reaches the surface of the butter.

It might be argued that gravity was acting through a greater distance in the case of a sample which was penetrated 30 mm. than in the case of one which was penetrated, say only 15 mm.; or again, it might be argued that the amount of friction on the sides of a small needle would be proportionately greater than that on a larger needle, on account of the greater area in proportion to its volume. These objections, if

they are applicable, would tend to counteract each other; and at any rate their influence is not perceptible in the results; for, duplicate determinations carried out with varying sizes of needles and weights, where the depth of penetration is necessarily greater in some cases than in others, show no greater variations than occur when the same sizes of needles and weights are used throughout, provided combinations which render readings difficult to make be avoided.

In practice we endeavor to secure a combination of needles and weights which will give a penetration of about 25 or 30 mm. and with our wide range of weights, 200 to 1400 grams, have ordinarily found it necessary to make use only of the needles having sectional areas of 25 and 50 sq. mm., when working at ordinary temperatures.

While the agreement of duplicate readings is not as close as is ordinarily expected in quantitative chemical work, it is, considering the nature of the determination, reasonably satisfactory when the samples have been properly prepared. The extreme variations rarely exceed 2 or 3 millimeters with a penetration of 25 to 30, and in the majority of cases, the readings have a closer agreement than that mentioned above. In practice we have taken the average of five or six readings as the final result. After the samples are prepared, we have been able to make and record from 40 to 50 readings per hour.

Since the end to be attained in this work was knowledge regarding the properties of the fat itself as distinguished from those properties which may have been introduced in the process of manufacturing the fat into butter, the hardness, like the other physical and chemical constants, has been determined on the rendered fat. Data have been introduced in Table 8 showing the hardness of several samples of butter prepared in different ways; also the hardness of the rendered fat from the same butter.

The method of procedure adopted in working with rendered butterfat is as follows: About 200 cc. of the mixed melted fat are placed in a 250 cc. Griffin

Table 1—All the Samples Shown in Table 1 were Taken from the Same Large Dish of Melted Butterfat which had been Thoroughly Mixed, and were Identical in Composition. After Being Poured into the Small Jars in which the Hardness was Measured the Samples Received the Same Treatment in Every Respect, Except that the Samples so Designated were Stirred with a Glass Rod as Described Elsewhere in this Paper, while they were Being Cooled in a Pan of Running Water. The Samples Designated as Unstirred were not Disturbed Until they were Solid. The Samples were All Removed at the Same Time to the Constant Temperature Bath and Kept at Almost Exactly 15° C. for 18 Hours.

Stirred while cooling		Not stirred	
Sample No.	Penetration	Sample No.	Penetration
1.....	21.0 mm.	8.....	28.0 mm.
2.....	22.0 "	9.....	24.0 "
3.....	22.5 "	10.....	29.0 "
4.....	23.5 "	11.....	25.0 "
5.....	22.0 "	12.....	28.0 "
6.....	23.0 "	13.....	27.0 "
7.....	22.0 "	14.....	24.0 "
		15.....	25.0 "
Average.....	22.1 "		
		Average.....	25.8 "

shape aluminum beaker which is set in cold water, 10 to 20° C. in a pan having a smooth level bottom. The fat is frequently stirred with a glass rod until

the rod can just be removed without leaving an impression in the fat. The sample is allowed to stand in the water a few minutes longer until it is well solidified. The stirring is done to prevent the separation of the fat into zones of different hardness, a condition which occurs when the melted fat is left to solidify without stirring. Tables 1, 2, 3 and 4 show data illustrating the effect of stirring on the observed hardness of the fat. It will be noticed that the penetration in the case of the unstirred samples, Tables 1 and 2, was

Table 2—This Data is of the Same Nature as that Shown in Table 1, the Samples Having Received Practically Identical Treatment to that Given the Samples in Table 1. The Butterfat Tested, however, was from a Different Source.

Stirred while cooling		Not stirred	
Sample No.	Penetration	Sample No.	Penetration
1.....	12.5 mm	9.....	18.5 mm
2.....	12.5 "	10.....	16.0 "
3.....	12.5 "	11.....	16.0 "
4.....	12.0 "	12.....	18.0 "
5.....	12.5 "	13.....	19.5 "
6.....	13.5 "	14.....	18.5 "
7.....	13.5 "	15.....	17.5 "
8.....	12.5 "		
Average.....	12.7 "	Average.....	17.7 "

greater on every occasion than with the stirred samples, due doubtless to the fact that in the small vessels employed to contain the fat, the penetration invariably took place near the center where the softer portions of the fat were collected.

It will be observed from Table 3 that when the samples were stirred during the process of cooling, the pene-

Table 3—Fat in Large Containers (600 Cc. Griffin Beakers). Samples were All Stirred While Cooling. No Effort was Made to Have Samples 1, 2, 3 and 4 of the Same Composition. Samples were Held at about 15° C. in the Constant Temperature Bath for 18 Hours.

Penetration in mm. at center 1 determination only		Penetration in mm. near edge Average of 4 determinations	
Sample 1.....	20.5	Sample 1.....	18.6
2.....	27.0	2.....	25.5
3.....	30.5	3.....	30.7
4.....	30.5	4.....	29.7

tration was practically the same regardless of which portion of fat was penetrated. In the case of the unstirred samples, Table 4, the penetration was much greater when measured at the center than when measured near the edges of the receptacle. The penetration measured midway between the center and edge

Table 4—The Same Conditions Obtained Here as Described for the Samples in Table 3, Except that None of the Samples were Stirred during the Cooling Process.

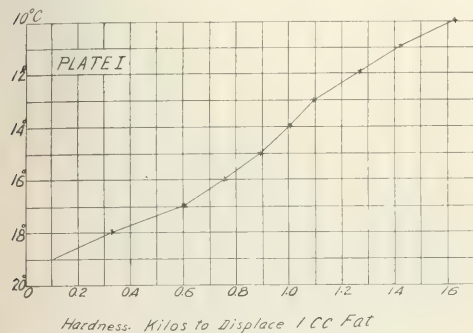
Penetration in mm. at center 1 determination only		Penetration in mm. near edge Average of 4 determinations	
Sample 1.....	30.5	Sample 1.....	22.1
2.....	30.5	2.....	22.0
3.....	29.5	3.....	21.8
4.....	29.0	4.....	20.8

was just about the average of that obtained at the center and that obtained at the edge. Stirring the fat in this way while it is cooling makes unnecessary a strict observance of rules 4, 5, and 6 as laid down by Sohn and quoted above.

The samples prepared in this way are transferred to a covered water bath tightly packed with heat insulating material inside a double walled wooden box. They are held here for 12 hours (over night) or longer

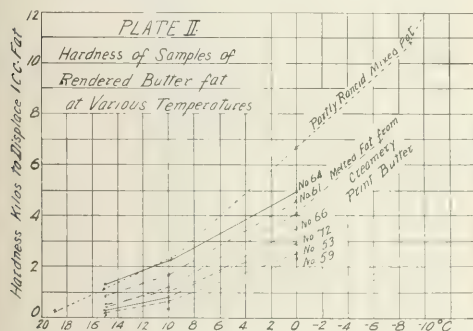


at a temperature not more than  $1^{\circ}$  C. from that at which the tests are to be made. The temperature is then adjusted to exactly the proper point and not allowed to vary more than  $0.1^{\circ}$  C. from that temperature for 6 hours before the tests are made. Samples held under these conditions gave much more uniform and satisfactory results than we were able to secure on recently solidified samples. The method of procedure in making the determination itself has already



been given as a part of the description of the apparatus.

Sohn in the article quoted above emphasized the importance of a close temperature control, and we have likewise found this absolutely essential, if results of any value are to be expected. The necessity of such a close control over the temperature can be better understood after a study of the results recorded



in Tables 5 and 6 and Plates I and II showing the hardness of several samples of fat at different temperatures. These results show clearly that a difference in temperature of even  $0.1^{\circ}$  is a very important matter when attempting to measure the hardness of fat.

It will also be noticed that the rate of increase in hardness, due to temperature, is considerably greater at lower temperatures than it is near the freezing point of the fat, which in the case of butterfat, is in the vicinity of  $20^{\circ}$  C. These results also serve to illustrate the well-known fact that there is a marked difference in hardness due to the individuality of the animal producing the fat. The numbers in Table 6 and Plate II correspond to the herd number of the animal producing the sample. These were selected at random

from cows in the dairy herd at the Ohio Experiment Station and by no means represent extremes.

Table 5—Showing the Hardness of the Same Samples of Butterfat at Temperatures Ranging from  $10^{\circ}$  C. to  $19^{\circ}$  C. Each Value as Stated was Calculated from the Average of Several Determinations Carried Out According to Our Regular Method of Procedure as Given Elsewhere. Hardness in Terms of Kilos Required to Displace 1 Cc. of Fat at Stated Temperatures.

Temperature	Hardness	Temperature	Hardness
$10^{\circ}$	1.630	$15^{\circ}$	0.890
$11^{\circ}$	1.420	$16^{\circ}$	0.750
$12^{\circ}$	1.270	$17^{\circ}$	0.603
$13^{\circ}$	1.092	$18^{\circ}$	0.337
$14^{\circ}$	1.012	$19^{\circ}$	0.113

Other factors such as breed, the advance of the period of lactation, and the character and amount of food, are supposed to have considerable influence on the hardness of the fat. The available data on certain of these points is well summed up by Hunziger, Mills, and Spitzer.<sup>1</sup> As already stated this method and apparatus were devised as a means of studying certain of these factors.

For general work with this method the most satisfactory temperature to be used in making determinations of the hardness of butterfat is probably that temperature between  $15^{\circ}$  and  $0^{\circ}$  C., which can be maintained with the greatest ease and constancy under available conditions. Any temperature above  $15^{\circ}$  C. will probably be too warm to permit an accurate determination of the hardness of soft samples of butterfat. In some ways the results secured at  $10^{\circ}$  C. or  $0^{\circ}$  C. are more satisfactory than those to be obtained at higher temperatures, because in working with the greater values the chances for error are lessened.

Table 6—Showing the Hardness of Several Samples of Butterfat at Different Temperatures. The Numbers Correspond to the Herd Number of the Animal Producing the Sample.

Temperatures	$19^{\circ}$ C.	$15^{\circ}$ C.	$10^{\circ}$ C.	$0^{\circ}$ C.	$-5^{\circ}$ C.	$-10^{\circ}$ C.
53.....	0.20	0.65	2.53			
59.....	0.12	0.38	2.33			
61.....	0.84	1.65	4.60			
64.....	1.27	2.25	5.00			
66.....	0.26	0.82	3.54			
72.....	0.56	1.02	2.93			
Melted fat from Creamery print butter.....	0.43	1.18	4.11	7.08		
Sample of mixed fat. Partly rancid.....	0.21	1.11	2.41	6.66	10.8	12.0
			(9 $3^{\circ}$ C.)			

The relative hardness of the samples at these temperatures may not, however, always represent their relative hardness at higher temperatures as shown by the data in Plate II and Table 6; and the fact must not be lost sight of, that from a practical standpoint the hardness of butter at  $0^{\circ}$  C. or even  $10^{\circ}$  C. is of little significance; while the hardness of butter at temperatures above  $15^{\circ}$  C. is a very important matter, for a butter which will stand up well and retain its hardness under summer conditions is greatly to be desired; such butter is especially demanded for export to tropical countries. Hunziger, Mills, and Spitzer<sup>1</sup> present evidence to show that the hardness of the fat is a very important matter which must be taken into account in regulating the water content of butter.

<sup>1</sup> Bull. 159, Purdue University, Agricultural Experiment Station.

In our work with rendered butterfat below  $10^{\circ}\text{C}$ . we have found it necessary to melt and remove a thin layer of fat from the outer edges of the container to prevent the formation of cracks throughout the sample, due to the contraction of the fat on cooling, since these interfered seriously with the determination. This was accomplished by wrapping the sides of the container of well solidified fat for a few seconds with a towel wrung out of hot water, and pouring out the melted fat. This gave a solid block of fat which did not crack when cooled. At  $-10^{\circ}\text{C}$ ., or below, the fat samples are inclined to split, when penetrated by the needle, like a block of free grained wood struck with an ax, and we were unable to secure satisfactory results at lower temperatures.

Most of our work has been done either at  $10^{\circ}$  or  $15^{\circ}\text{C}$ . During the greater part of the year it has been found practicable to maintain the latter temperature quite satisfactorily in an unheated basement room with the equipment which has already been described. This can be done whenever the room temperature is reasonably constant and is not more than  $2^{\circ}\text{C}$ . in either direction from the temperature to be maintained. A constant temperature room or apparatus is very desirable when either can be had. We have used with great satisfaction rooms in the cold storage plant at the Ohio Experiment Station in securing part of the data contained in this paper. A temperature of  $6^{\circ}\text{C}$ . can be maintained quite satisfactorily in a room several degrees above that temperature by keeping the insulated water bath well supplied with crushed ice.

Statements made by certain of the investigators named above suggested that previous exposure to heat or cold might permanently affect the hardness of the butterfat. To determine whether such was the case, a large number of samples of mixed fat were prepared and treated under much more rigorous conditions of both heat and cold than those which need ever be met with in carrying out determinations by this method. Part of these samples were held at different times for from 48 to 96 hours at a temperature approximating  $10^{\circ}\text{F}$ . Others were heated at  $95^{\circ}\text{C}$ . on a steam bath for periods of 48 hours; others were held at  $15^{\circ}\text{C}$ ., the temperature at which all were tested. At the conclusion of the special treatment, all were treated according to the usual method described elsewhere in this paper. These results are given in Table 7. They seem to show that neither heat nor cold within the limits encountered in operating this test have any marked permanent effect on the hardness of butterfat. Likewise samples which we have repeatedly heated and cooled in obtaining other data contained in this paper have shown no change of hardness in the process.

In working with manufactured butter, results can be obtained which duplicate each other more closely than the results secured on the rendered fat; also less care is required in the preparation of the samples. The butter under examination was either in the form of 1 pound prints or was well packed in the 250 cc. aluminum beakers already referred to, and immersed in the constant temperature bath in the same manner

as described for samples of rendered fat. At first thought, it would seem that data regarding the hardness of fat could be obtained to better advantage on the manufactured butter than on the rendered fat itself. Some of the investigators referred to above have followed this method. While we have not extended our investigation to include all of the details of the manner in which the hardness of manufactured

Table 7—Showing the Hardness of Several Samples of Butterfat of Uniform Composition, Exposed to Excessive Conditions of Heat and Cold. Penetration in Mm. All Other Conditions Constant. All Kept in Insulated Water Bath at  $15^{\circ}\text{C}$ . for 24 Hours before Testing.

Group 1 Held at approximately 10 F for 48 hrs. or more			Group 2 Held at $15^{\circ}\text{C}$ .			Group 3 Heated on steam bath at $95^{\circ}\text{C}$ for 48 hours		
22.0	23.0		24.0	20.5	20.0	20.5	24.5	20.5
23.0	20.5		23.0	22.5	19.0	21.0	24.5	20.5
22.5	22.0		23.5	23.0	19.0	23.5	20.0	24.0
23.0	21.0		19.5	23.0	21.0	20.5	20.5	21.0
24.0	20.5		23.0	22.5	21.0	22.5	20.5	20.0
23.0	20.0		21.0	25.0	21.0	21.0	20.5	20.5
21.0	20.5		21.5	21.5	20.0	22.0	21.0	21.0
21.0	22.5		20.0	22.5	21.0	21.5	20.5	21.0
24.0	20.0		24.5	24.5	21.0	22.0	20.0	21.5
23.0	20.5		25.5	25.0	21.0	21.5	20.5	21.0
20.0	20.5		20.0	19.0	20.0	23.0	22.5	21.5
19.0	21.5		23.5	19.0	20.0	20.0	20.5	
22.5								
Average, 21.6			Average, 21.6			Average, 21.4		

butter may be affected by the methods employed during its manufacture, the results given in Table 8 clearly show that the hardness of the fat as determined in this way will probably be very greatly influenced by differences of method in preparing the butter. This data taken in connection with that given in Table 6 and Plate II indicate that the differences in observed hardness due to this cause may readily be fully as great as those due to the properties of the fat itself.

Table 8—Showing Hardness of Several Samples of Butter Prepared in Different Ways. Also of the Melted Fat from the Same, Hardness = Kilos to Displace 1 Cc. Fat.

Conditions under which the different portions of the samples were prepared	Dairy butter Sample 1	Dairy butter Sample 2	Dairy butter Sample 3	Creamery print butter
C. temperatures at which tests were made.....	$10^{\circ}$	$10^{\circ}$	$10^{\circ}$	$15^{\circ}$
Original butter or butter worked and packed under about the usual conditions.....	0.42	0.35	0.55	0.11
Butter excessively worked while soft.....	0.63	0.44	0.56	0.19
Butter excessively worked while hard .....	0.16	0.14	0.28	0.07
Rendered fat from the same butter	1.15	0.76	0.84	0.44

It occurs as a probable explanation of the above described phenomena that the crystalline structure of the soft worked butter is developed by this treatment, while that of the butter worked excessively while hard is broken up thereby. The soft worked butter possessed a high luster while the hard worked butter had a dull lusterless appearance, which may be regarded as further evidence in support of the above view.

Under the microscope the solidified rendered fat presented a well defined crystalline structure. The butter worked somewhat excessively while hard showed no evidence of crystal formation but appeared in masses

of varying size all rounded. The butter worked excessively while in a soft condition seemed to have a structure intermediate between that of the hard worked butter and that of the solidified rendered fat, both rounded masses and crystals being in evidence.

This method should be of service to the butter-judge under certain conditions where an accurate judgment regarding the body of butter is especially desired. It should be particularly useful in laboratories where detailed examinations of the properties of fats, oils or lubricants are carried out. The apparatus itself with certain modifications should be useful for determining the penetrability of asphalt, the setting point of cement, or for any purpose where an accurate penetration test is desired.

#### CONCLUSIONS

1. This method is the most accurate that has yet been described.
2. It is necessary to stir the samples while cooling to prevent separation into zones of different hardness.
3. The temperature has a very marked effect on the hardness of the butterfat.
4. The sample should be kept at a constant temperature for 6 hours or more before testing.
5. The temperature to which the fat had previously been subjected seemed to make no difference in the hardness provided the samples were treated as described.
6. The determinations can be made with great rapidity after the samples are properly prepared.
7. More closely agreeing duplicate determinations are procurable with this method in examining manufactured butter than in examining the rendered fat.
8. The results obtained, however, are likely to be very greatly affected by variations in the method of preparing the butter; they probably will not truly represent the properties of the fat itself.
9. The apparatus with slight modifications should be useful for other work of a similar nature.

The writer is indebted to Mr. R. H. Shaw for the use in a preliminary way of an unpublished piece of apparatus designed by him for the same purpose; and to Prof. C. H. Eckles and Dr. Matthew Steel for valuable advice and suggestions. The apparatus was designed and part of the work done while the writer was employed in the laboratory maintained jointly by the Dairy Division, United States Department of Agriculture, and The Missouri Agricultural Experiment Station, at Columbia, Mo. Additional work has been done in the laboratory of the Dairy Department of the Ohio Agricultural Experiment Station, Wooster, Ohio.

NOTE.—The original apparatus still in use at the Missouri Station was constructed for the writer by Mr. Emil Klinkerfuss, mechanic at the University of Missouri. A duplicate apparatus for use at the Ohio Experiment Station has been constructed by Eimer and Amend.

#### INFLUENCE OF SMALL AMOUNTS OF ETHYL ALCOHOL ON FERMENTATION IN CANE SUGAR SYRUP

By C. B. COCHRAN<sup>1</sup> AND J. H. PERKINS<sup>2</sup>

Received October 17, 1913

Preparatory to determining the preservative values of a variety of compounds, we made them up into standard alcoholic solutions. The volume of the solution containing the amount of the compound desired was mixed with a definite amount of simple syrup, which then contained, in addition to the added compound, a small amount of alcohol. In several instances, we noted that yeast did not act on these syrups exactly as they did on similar syrups containing no alcohol. We then carried on the following experiments in order to determine just what influence a small amount of alcohol has on fermentation in cane sugar syrup.

Simple syrups, ranging in specific gravity from 1.2112 to 1.26 at 20° C., were made by dissolving granulated cane sugar in warm—not hot—water. Sufficient alcohol to make the percentage desired was then added to each syrup, some of the syrup, however, being kept for blank or control tests.

These syrups were then tested as follows: one thirty-second of a Fleischmann's yeast cake was thoroughly mixed with one fluid ounce of syrup, with the exception of the 1.245 syrups, to 50 cc. of which one-sixteenth of a yeast cake was added. Portions of the syrup were then put in two fermentation tubes and kept in an incubator at between 31 and 32° C. The percentage of gas was noted daily. When the two tubes contained the same amount of gas, the result is not stated in duplicate.

The percentage of absolute alcohol is given by volume.

Per cent alcohol by vol.	Sp. gr. 20° C.	Syrup	Time Days	Per cent of gas	Per cent alcohol by vol.	Sp. gr. 20° C.	Syrup	Time Days	Per cent of gas
0.033	1.259	1	100	None	1.2558	1	70		
None	1.259	1	55 & 78	2	100	2	100		
0.658	1.2572	1	100	1.633	1.25544	1	45 & 42		
None	1.2572	1	22	2	100	4 a)	80 & 83		
		4 a)	100	1.88	1.2514	1	65 & 80		
0.77	1.2112	1	20 & 30	2	100	2	100		
		2	80 & 100	None	1.2514	1	70 & 80		
None	1.2112	1	15	2	100	2	100		
		2	100	1.88	1.26	1	15 & 35		
1.0	1.2563	1	65 & 70	2	80 & 100	2	100		
		2	100	None	1.26	1	45 & 55		
None	1.2563	1	20	2	100	2	100		
		2	53	2.0	1.245	3	75		
		4 a)	100	None	1.245	2	100		
1.25	1.2558	1	60 & 70	3.0	1.245	3	30		
		2	100	5.0	1.245	4	3		

(a) The third day being Sunday, no reading was made.

CONCLUSIONS.—I. One per cent or less of alcohol markedly accelerates fermentation in syrup of above densities.

2. 1.25 per cent of alcohol has very little influence.

3. Beginning with 1.25 per cent the presence of alcohol retards fermentation in these syrups; the amount of retardation increasing with the increase in the percentage of alcohol.

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<sup>2</sup> Chief Chemist for the Charles E. Hires Company.



## LABORATORY AND PLANT

### FILTER PRESSES<sup>1</sup>

By E. J. SWERDLOFF

That there is great room for improvement in the methods of filtration commonly employed cannot be doubted. The plate and frame filter press ordinarily used comprises anywhere from 40 to 100 filter chambers, each of which must be cleaned individually by hand every time the filter is filled.

It was to eliminate the excessive amount of hand labor in cleaning filter presses that the filter under discussion was primarily designed, but as the construction was developed many incidental advantages of importance developed with it, as will be pointed out further on.

The single advantage in plate and frame filter presses that has kept them in favor is the fact that their peculiar construction affords a very large filter area in a comparatively small space. Filtration cannot be forced beyond a certain reasonable limit; when this limit is reached, it is necessary to increase filter area to increase capacity. To endeavor to increase capacity by increasing pressure instead of filter area is futile, for excessive pressure merely presses the cake to a compact, almost impervious layer and the object is defeated at once.

With this in view, the modern filter must not depart from a construction that permits of ample filter surface. Other things being equal, the capacity, and consequently the value, of a filter is proportional to the filter area.

The sluicing type of filter press is one example of a filter press construction that eliminates hand labor in cleaning. In this type the cake is disintegrated by a stream of water forced into each chamber. The cake thus liquefied flows to the waste reservoir, or dump. The usefulness of this method is limited for obvious reasons, chief of which is the need of recovering the cake as dry as possible in most processes.

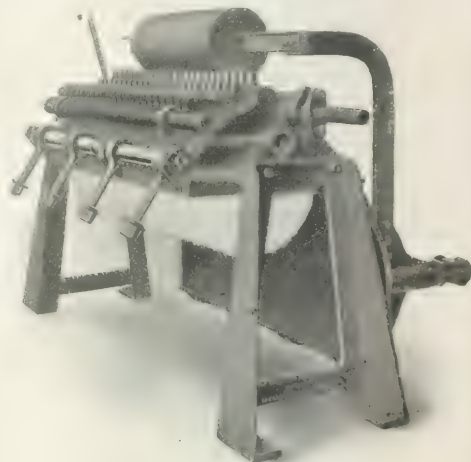
The uses of filter presses are so varied that great flexibility is required. One process will demand a filter capable of handling a thick sludge containing twenty or thirty per cent solids, forming cakes probably four inches in thickness, which have to be thoroughly washed; the next problem may consist of clarifying a viscous fluid containing but traces of solids, so finely divided as to make a thick cake an impossibility. One problem calls for recovery of the solids only, the filtrate being of no value, while another rejects the solids as refuse after recovering the liquid content; still another requires recovery of both liquid and solid. Some plants make certain products at certain seasons only and must use the same filter press for an entirely different product at other seasons. To be a commercial success it would seem that the modern filter press should lend itself to these various require-

ments and the construction be made adjustable as far as possible.

As will be seen from the following description, the filter under discussion is a radical departure from the plate and frame filter press and is even more simple in construction.

### CONSTRUCTION

This filter has become known as the "clam-shell" type due to the shell being in two parts hinged together to open and close somewhat after the manner of the clam-shell bucket used on steam shovels.



COUNTER-WEIGHTED PRESS OPEN

The filter body comprises two semi-cylindrical members hinged together, one member being provided with an inserted gasket which seals the joint between the two to form a water-tight cylinder when closed.

A plurality of openings is provided along the top to receive the stem or outlet nipple of the filter leaves. These outlets are spaced quite close together so that the leaves may be closely spaced if desired, as is the case when thin cakes are to be formed; but the leaf spacing may be increased to any degree by taking out part of the leaves and stopping off the intermediate outlets.

Variable spacing is quite essential, for it is not always possible to ascertain in advance exactly what spacing will be best suited to the material; and further, there is always the possibility of the process being modified to change the filtering properties of the material and make a change in leaf spacing desirable.

The filter leaves are usually made of wire screen, well crimped to provide ample drainage. The screen is bound at the edges to stiffen the construction and protect the cloth. An outlet nipple with a side open-

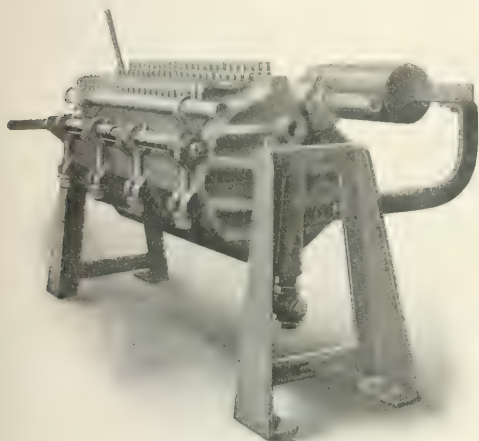
<sup>1</sup> Presented at the 6th Annual Meeting of the American Institute of Chemical Engineers, The Chemists' Club, New York, December 10-13, 1913.

ing furnishes an exit for the filtrate and means of holding the leaf in the filter body. The filter cloth covers the entire metal construction of the leaf except the outlet nipple and is held on either with metal clips or by being stitched around the edges.

The leaves are held in place in the filter by a cap nut which engages the top of the nipple and draws the shoulder of the leaf tightly against the rubber washer which fits in a recess inside the filter body. The side outlet of the nipple aligns with the filtrate delivery fittings on the outside of the press.

The accompanying cross-sections of the filter body clearly show how the filter leaves are held in place

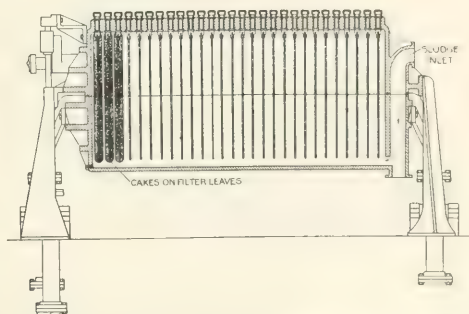
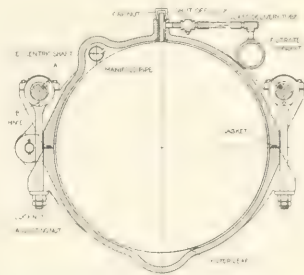
seemed the great problem in working out this improvement was the need of accurate hinge adjustment to take up wear in the gasket. This problem like many mechanical problems proved to be simpler than was anticipated, for it was solved by simply making the hinge pins into one continuous shaft reaching from end to end of the press, and turning the bearing which received all of the hinges on the upper member eccentric to the normal axis of the shaft. This construction not only affords adjustment, but makes



COUNTER-WEIGHTED PRESS CLOSED

by the nipple at the top. Each leaf has separate outlet fittings comprising shutoff cock, glass delivery tube, etc. These fittings allow the operative to see the filtrate from each individual leaf as it flows through the glass, and any leaf that might become injured or require renewal of cloth is indicated at once by a turbid filtrate in the glass. In this event the shutoff cock governing the defective leaf is closed until the filter is opened and the leaf replaced. To remove a leaf only the cap nut has to be removed—the outlet fittings are not disturbed.

In the earlier designs of this filter the two halves of the shell were held in closed position by hand-operated swing bolts. These were fairly quick and convenient to operate but still left room for improvement. It was desired to modify the construction to an extent that would reduce the time to unlock and open the filter from a few minutes to a few seconds, if possible. This was accomplished by a very simple change in the construction. The hinges, which formerly took no strain while the filter was in locked position, were increased in strength and number and made to take the strain formerly taken by the swing bolts on the back of the filter body. To eliminate any possibility of breakage, the hinges are made of steel, which can be fully depended upon for strength. What



CROSS AND LONGITUDINAL SECTIONS OF SWEETLAND FILTER PRESS

adjustment of all hinges simultaneous by merely turning the hinge shaft slightly when adjustment is necessary to draw the upper and lower halves of the shell closer together as the gasket gradually flattens out from continued use. The shaft is held from turning by set screws, which are loosened when adjustment is made.

An eccentric shaft with swing bolts rests in babbitted bearings along the front of the upper half. Each bolt has an adjusting nut and lock nut for initial adjustment and for taking up wear. The swing bolts are tightened or loosened simultaneously, due to the eccentricity of the shaft, when the latter is turned through an arc of  $180^\circ$ , and means is provided for swinging the bolts clear of the lugs on the lower half just at the point when they have loosened sufficiently to disengage themselves.

This arrangement makes it possible to open or close a filter press of moderate size in a few seconds. The lower half of the shell is poised with counterweights to facilitate opening and closing.

In large machines an eccentric shaft is used on both front and back, and a hydraulic cylinder operates the two simultaneously by means of a crosshead and connecting rods. The lower member in this case is swung open and shut by a hydraulic cylinder at either end which is so arranged that the shell is opened so wide as to invert it and thus clean itself of any cake that might have fallen before it was fully opened.

#### OPERATION

In operating the filter the liquid to be filtered is forced into the filter body under pressure, expelling the air and entirely submerging the filter leaves. The liquid filters through the cloth and deposits the suspended solids on the outside of the leaves, forming the "cakes." Filtration continues until the cakes on adjacent leaves are separated only by a narrow space which may vary in width from  $\frac{1}{8}$  inch upward. When the cakes are formed to the proper thickness the wash water valve is opened and the sludge valve closed simultaneously. The wash water enters

testing samples of the washed cake from various parts of the press.

All filters of the leaf type wash by "direct contact" methods; that is, the wash water is in direct contact with the cake; but the methods of washing that have heretofore been practiced with leaf filters whether vacuum or pressure are indeed anything but direct.

The usual method of forming and washing the cakes on filter leaves is as follows, assuming that the cake has to be washed first with weak liquor and then with water:

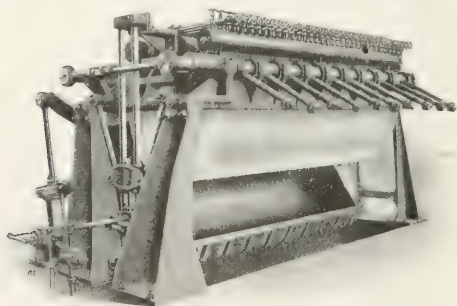
- 1st. Fill filter tank.
- 2nd. Deposit cake on leaves.
- 3rd. Withdraw excess solution.
- 4th. Fill filter tank with weak solution.
- 5th. Wash cakes with weak solution.
- 6th. Withdraw excess weak solution.
- 7th. Fill filter tank with water.
- 8th. Wash with water.
- 9th. Withdraw excess water.
- 10th. Discharge cakes from leaves.

Here are ten distinct operations, which are still further complicated by the fact that the cakes will not cling to the leaves unassisted, but must be held on with either compressed air or vacuum during the time each quantity of excess is withdrawn. I do not dispute that the cakes can be washed well by this method, but raise the point that it is an extremely round-about method of accomplishing a simple object. Most of the power consumed is not devoted to filtration but to transferring solutions, much of the time is not devoted to filtering but to waiting for transfers to be made, and the operator is kept busy manipulating valves.

The delay in filtering necessitated by the many transfers materially cuts down the duty of the filter, and the process becomes a complicated one, requiring many tanks and much accessory apparatus to take care of excess solutions.

Nor is this all. The transfers of excess solutions referred to introduce other complications. The cakes must be supported upon the leaves at all times by pressure. Air pressure (whether produced by suction or otherwise) must be used during the transfers. If too much pressure is used, the cake will be cracked (due to the shrinkage of partial drying) and the wash water will "short-circuit," that is, pass through the channels formed by cracking. If too little pressure is used, all or part of the cakes may fall from the leaves, which would preclude the possibility of efficient washing. Lastly, if the cakes are of a slimy character, the partial drying during the transfer packs the particles of slime, and makes it less pervious than ever to the passage of wash water.

The origin of the many complications cited above is traced directly to void or "dead" space in the filter tank or chamber which contains the filter leaves. If there were no dead space, there would be no excess solutions, and consequently none of the complications which attend them.



HYDRAULICALLY OPERATED PRESS OPEN

the space between the cakes, forcing the small quantity of unfiltered sludge to deposit its solid component upon the cake surface. The space between adjacent cakes is now occupied by water which, being under pressure, percolates through the cakes, driving the strong liquor ahead and effectively displacing it until the cakes are washed to the desired degree, which is indicated by frequent tests of the effluent.

I feel justified in enlarging somewhat upon the subject of washing the cakes, for therein lies a great difference between this and other leaf filters. It should be noted that there are no chambers or containers to be packed solidly full of cake. The spaces between the leaves are not packed solidly full, but a cake is deposited on the surface of each leaf and these cakes are allowed to build up until only a narrow space remains between them, and in this space lies the secret of successful automatic discharging of the filter, and efficient washing. The cakes have been formed under equal conditions, the sludge being evenly distributed and the pressure equal throughout the filter chamber; therefore, the cakes must be of even thickness and density and must wash evenly. That this actually occurs has often been demonstrated by



The "clam-shell" construction of filter body has no void spaces. It contains nothing but the filter leaves and manifold pipe. When the filter leaves are loaded with cake, the entire filter chamber is full except the feed channel for distribution along the bottom, and the narrow space between the cakes for the entrance of wash water. There is, therefore, no excess solution to handle. Filtration is continuous from the time cake-forming is commenced until washing is finished, and the process of filtering and washing is reduced to the simplest possible form.

When washing is finished, the cakes are partially dried with compressed air, the lower half of the filter body is swung open and the cakes are dumped into a car or conveyor underneath. To assist the cakes to dislodge from the leaves, the current is reversed by turning steam or compressed air inside of the leaves, which not only causes the cakes to drop off, but benefits the cloth by keeping the pores open.

For the benefit of those who insist that better washing can be obtained by draining the filter body before introducing wash solutions or water, I would point out that the filter construction here described offers every facility for carrying out this method, if desired; but after installing many of them, large and small and under widely varying conditions, and seeing trials made both ways, I strongly advocate the direct method without withdrawing solutions.

If the material is very slow-filtering and the space between the cakes wide, then it is better to introduce the wash water through the manifold pipe and let the water entering the top fill the chamber by downward displacement, forcing the excess solution out of the drain valve at the bottom. The water, being lighter than the sludge, does not mix with it, but floats on top during displacement. In this case filtration is continuous, pressure is maintained in the chamber, no time is lost, and the cakes are constantly submerged.

It is so frequently asked why the body of this filter was designed cylindrical instead of square that I shall take this opportunity to point out the reason. Obviously the principle could be carried out in a filter body of square or rectangular section. The reasons for cylindrical construction are:

1. The cylindrical construction affords great strength whereas any shape with straight sides would require so much reinforcement to give it the necessary strength as to make it cumbersome and awkward.
2. The leaves are exposed to view by simply swinging the body open.
3. A circular leaf is conveniently supported from one point and is very strong and light.
4. If the chamber were square, the leaves would be inaccessible, or else would have to be lifted out with the cover to discharge, and this would involve mechanical difficulties.

The circular form of leaf does not involve as much waste in filter cloth as might be imagined. There is to be sure a slight waste of cloth cut from the corners but most of this has an important use in reinforcing

the cloth at the edges of the leaf; on the other hand, a large percentage of the cloth used in plate and frame presses is not used for filtering, but to form a joint between the frames. If we figure it out in any case, we find the percentage of cloth purchased that is utilized as filter medium, is about the same for either shape. In fact, the cost of cloth per unit of work done is much less in the case of the leaf construction, because the capacity per square foot is greater, and the cloth is not injured by being squeezed between the frames.

As to filtering mixtures containing coarse particles, these offer difficulty in any type of filter, due to the coarse particles settling to the bottom, making the bottom of the cakes more porous than the top and resulting in uneven washing. The remedy for this trouble is to keep the contents of the filter chamber in a state of agitation. To accomplish this, the feed pump is provided large enough to supply the necessary pressure for filtration with additional capacity enough to permit a restricted overflow to run from the manifold pipe back to the supply tank during filtration.

New light is being thrown on the subject of filtration with almost every new installation, and problems are being successfully solved that appeared at the start to be impossible of solution. To cite an instance: a sample of a heavy viscous liquid was submitted for test. It contained a gummy residue that blocked the filter cloth from the start, the rate of flow of filtrate per square foot of cloth was but a few cubic centimeters per hour, and the cloth became so coated as to defy cleaning by any practical method. As the solution only was required, and the residue was worthless, there seemed to be no objection to adding some inert granular substance to the liquid as an aid to filtration. A series of experiments was undertaken, adding various "filter aids" to the fluid, and the outcome of this work was that an average rate of filtration of three gallons per square foot of cloth per hour was obtained and the gummy residual matter was sufficiently broken up to permit the filter cloth to be readily cleaned by reversal of current. Upon completion of the tests, a filter was installed in the plant and has fully demonstrated the practicability of the method on a working scale. It was found that any one of several substances could be used as an aid to filtration, among which are fine sand, fuller's earth, kieselguhr, sulfate or carbonate of lime, sawdust, wood pulp, etc.

It is not argued that such methods are applicable to all cases, but there are unquestionably many problems that will find solution in similar schemes, which make possible rates of filtration such as are usually obtainable only in sand filters, with the added advantage that the leaf filter offers an enormous filter area in a small space, combined with extraordinary ease of cleaning.

Another method of filtering materials containing a gummy residue that tends to choke the cloth is that of depositing a protecting layer on the cloth before commencing filtration. For instance, we may

first fill the filter body with a very thin slurry of carbonate of lime and filter this mixture for a few seconds until a film of lime, say  $\frac{1}{32}$  inch in thickness, has been deposited. This coats the cloth as completely and evenly as a deposit could possibly be made. The lime slurry is then drained off and filtration commenced. The coating of lime forms a complete film between the cloth and gummy residue, so the latter never even touches the cloth. When ready to clean the cloth the reversal of current is effective because the coating of lime breaks away readily.

It is frequently asked how we can tell when cakes of sufficient thickness have been formed, especially when the material filters and builds up the cake rapidly. This is not as difficult as would be imagined. The usual way is to work at a given pressure, say forty pounds per square inch, and pump for a certain number of minutes, determined by practice to form the required cake. Another way is to pump a certain number of inches from the supply tank for each charge. As in all processes, the operative soon becomes expert, and can judge from the general conduct of the filter when the charge is sufficient.

The usual skepticism which attends the introduction of any new machine was encountered at first, but so many installations are now in successful use as to establish fully the usefulness of the methods described. A noteworthy point is the fact that many of the filters of this type in use are of much larger size and capacity than it is found practicable to build filter presses. Many have been built with a capacity of 133 cubic feet of cake per charge and several others ranging from 80 to 120 cubic feet per charge. One especially large one was built which dumps over 25 tons of cake per charge.

That this apparatus is now far beyond the experimental stages is demonstrated by the fact that a large beet sugar factory in California installed three large hydraulically operated machines for the 1913 campaign. They were installed almost at the last minute before the campaign started and were at once placed in service at full capacity, and no difficulty was encountered, in spite of the fact that none of the employees who operated the machines had ever seen one before. The time required to open, clean and close one of these filters is about five minutes, which minimizes labor to such an extent that one operator can take care of several large machines, even though each machine has to be cleaned hourly.

SWEETLAND FILTER PRESS CO.  
149 BROADWAY, NEW YORK

### IMPROVED MINE FIRES ON AN EXPERIMENTAL SCALE

Received January 15, 1914

The Bureau of Mines has recently installed at its Pittsburgh experiment station an underground chamber or furnace in which to carry on experiments relating to mine fires and spontaneous combustion as occurring in mines.

A section of steel tube cylindrical in shape, 6 $\frac{1}{2}$  feet in diameter and 27 feet long, was laid on its side

in a deep trench, and after lining this shell with firebrick and mineral wool and stopping the ends with 13-inch brick walls, it was covered with two feet of earth. The chamber was constructed so as to be as



SIDE VIEW OF "COMBUSTION OF COAL" APPARATUS

nearly air-tight as possible, and in such manner as to retain to the greatest degree practicable any heat generated within its walls.

At one end a motor-driven fan will blow in air at a rate which can be accurately measured, and at the other a stack is provided which can be opened or closed as desired. Through the top of the chamber, at frequent intervals, pass small pipes for withdrawing samples of air or gases and for inserting pyrometers for temperature measurement in the interior.

The chamber will hold 6 to 8 tons of coal when one-third full. It is expected that different kinds of coal or of the gob or waste material from mines will be placed in the chamber and a study made of spontaneous development of heat in them under various conditions. After an active fire has been started in the chamber



CROSS SECTION OF "COMBUSTION OF COAL" APPARATUS SHOWING METHOD OF CONSTRUCTION OF BRICK LINING

either by this means or artificially, experiments will be made on controlling the fire by reducing the air supply or by sealing it off entirely. The progressive changes in composition of the fire gases or of the air surrounding the coal will be followed and temperature measurements made, in an endeavor to apply the data

thus obtained to solving practical problems in the treatment of mine fires.

Investigations have been made in other countries and to some extent also in this country, of the gases produced in actual cases of mine fires both before and after sealing off a burning area. The bureau is now making, however, probably the first attempt to in-



"COMBUSTION OF COAL" APPARATUS SHOWING GAS AND AIR CONNECTIONS TO COMBUSTION CHAMBER

vestigate such problems in an experimental apparatus which permits careful control of conditions and yet is on a scale nearly commensurate with mining operations. These investigations are being carried on by Horace C. Porter, chemist, of the Bureau of Mines.

#### A SHAKER FOR THE MECHANICAL ANALYSIS OF SOIL

By FREEMAN WARD

Received October 23, 1913

**INTRODUCTORY.**—In the mechanical analysis of soil one of the prime requisites is the complete separation of all the particles before sorting them into groups or grades according to size. The tendency in the natural soil is for the finer particles either to gather among themselves as aggregates or to cling to the larger grains. If a complete separation is not effected the per cent of the finer grades of soil will be below, and that of the coarser grades above the truth.

The separation can be effected mechanically in one of two ways—pestling and stirring; or shaking, as advocated by the Department of Agriculture<sup>1</sup>—water (very slightly ammoniacal) being added in either case. The essential idea of the latter is to place bottles containing soil and water in a horizontal position in trays which are jerked backward and forward by means of an eccentric attachment.

The purpose of this article is to describe a different

<sup>1</sup> C. C. Fletcher and H. Bryan, "Modification of the Method of Mechanical Soil Analysis," U. S. Dept. Agr., Bur. Soils, *Bull.* 84, 1912.

type of shaker used by the writer and believed to have certain advantages.

**DESCRIPTION.**—The principle is as follows: The bottles with soil and water are ended over and over, thus allowing the contents to fall from one end of the bottle to the other. This is accomplished by having the bottles attached radially to a wheel which is rotated slowly in a vertical plane.

The machine used by the writer is "home-made" and consists of two small cart wheels sixteen inches in diameter, both on the same axle and touching hub to hub: this leaves the edges of the tires about three inches apart. Strips of tin fastened to the felloes serve not only to hold the two wheels together, but also with the felloes act as a broad groove ( $1\frac{1}{2}$  inches wide) for a belt to run on.

The bottles used are the kind known commercially as "four ounce sample oil bottles:" they are about six inches long and one and one-half inches in diameter, and are fitted with rubber stoppers: they have a capacity of 120 cc. The base of each is slipped into a sleeve of tin fastened near the hub: a wire clamp secures the bottle at the neck.

The wheel thus constructed will hold sixteen of these bottles arranged radially—eight on a side. It may be attached to a motor by means of a belt. Plate I is a photograph of the machine.

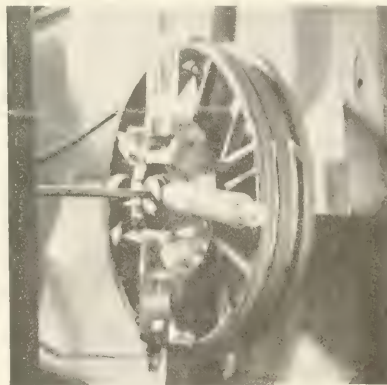


PLATE I

To operate—put weighed (10 grams) sample of soil in bottle; fill one-half full of water which is slightly ammoniacal; attach bottle to wheel and revolve at the rate of twenty-five revolutions a minute; let run for three hours.

**ADVANTAGES.**—Separation by stirring and pestling is too laborious, consumes too much time, does not always result in a clean separation and has a tendency to mechanically fracture the particles of soil. Both the shaker methods are not only safer, and more effective, but, since they can be run by machinery, are convenient. And in either case the removal of the grades silt and clay by sedimentation and decantation



can be undertaken directly after the shaking without transferring the whole sample to another vessel.

The writer believes that his method is better than the one used by the Bureau of Soils in two respects. In the first place the machine is simple and inexpensive. A greater advantage is the saving of time. Clean separations can be effected in three hours, and in some

cases two hours: this is a saving of at least four hours over the Bureau method. If the quantity of the water used in the bottles is reduced one-half, a clean separation results in much less than three hours, but there is a tendency for the grains to suffer some abrasion.

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## ADDRESSES

### THE PRESENT STATUS OF THE WOOD TURPENTINE INDUSTRY<sup>1</sup>

By E. H. FRECHET and JAMES R. WETBOW

In treating a subject that has as many phases as this one, it will be necessary to discuss briefly an allied industry, namely, that of Gum Turpentine as distinguished from Wood Turpentine, in order that the reasons calling for the development of this latter industry may be seen with the proper perspective.

That the Wood Turpentine Industry is at present at an extremely low ebb is unquestionably true. Nevertheless, it is likewise true that its scientific development is an economic necessity for certain localities, in order that waste may be conserved, that the products from waste replace those from the fast disappearing pine and fir forests and that cut-over land may be cleared at a profit instead of at a loss. Therefore, in this instance, as is often the case, necessity compels development.

The fact that thousands of dollars have been expended and lost in the incubation of this industry has been due, in our opinion, to three main causes, any one of which in itself would account for failure: *first*, the lack of practical scientific engineers experienced in this or analogous fields; *second*, financing for the sale of stock and securities rather than product; and *third*, lack of efficient marketing organization. It must also be borne in mind, that owing to the number of different processes, there was caused a lack of uniformity of product, which naturally tended to increase selling costs. Except to the U. S. Navy, little, if any, wood turpentine has been sold on thorough specifications. There has as yet been no real attempt by manufacturers to effect a general standard, although a few years ago the producers of the practically defunct steam process turpentine did make an attempt to standardize their product.

One of the important influences that tended at first toward the development of the industry and later proved extremely detrimental, was the speculative nature of the naval stores market. This was made up entirely of gum turpentine and rosin, upon the prices of which the relative wood turpentine values were determined. This market in the past has been subject to violent price changes, a fluctuation of from 30 cents to over \$1.00 per gallon having been experienced, which was due almost wholly to speculation. Naturally, therefore, during the upward swing of prices an unnatural development occurred, and plants using costly processes and with inefficient management were profitably operated and exploited. It followed, of course, that when the national government, through criminal prosecution, put a stop to excessive speculation, a corresponding reaction occurred, ruining many concerns which required abnormal prices for financial success.

Unreasonably high prices not only encouraged the development of the wood turpentine industry, but also caused an expansion in operations by the gum turpentine manufacturers so that a larger percentage of trees, and many very young trees, were boxed, causing overproduction.

### GUM TURPENTINE

The method of producing oil of turpentine from the resins of coniferous trees, consists in cutting a broad wedge-shaped notch or cup at the base of the tree and removing the bark immediately above the notch for about 18 to 24 inches. The resin exuding from the peeled area runs into the cup at the bottom and is collected from time to time. Each succeeding season the barked area is increased until it reaches about the height of one's head, usually taking five or six years. As many as four "boxes" are thus cut on one tree, depending on its size, permitting only enough of the original bark to remain to prevent the death of the tree.

After collecting sufficient quantity of the resin, it is distilled in a copper still, usually a "fire still," equipped with a live steam jet or a water supply. The turpentine thus produced is not carried farther in any refining process, but is ready for the market. The residue in the still is the rosin of commerce and is barreled at the still. The dross obtained by filtering sticks, dirt, etc., from the rosin is in many places being worked into cheaper grades of rosin. With rosin at an average price, it is generally figured that to make the operation profitable, about 42 cents per gallon must be obtained for the turpentine.

The marketing of the products is done through "factors" as they are called; that is, companies or individuals who contract with the producers for their output, supply them with funds for pay-rolls, etc., and advances when necessary. These "factors" take the product when produced, but usually have no other connection with the producer. Savannah, Georgia, is the leading naval stores center in the world and usually Savannah prices are accepted as the standard. Jacksonville and Pensacola, Florida, Brunswick, Ga., and New Orleans, La., are also large "factor" centers for this industry.

This method of producing turpentine is generally conceded to give the best turpentine and rosin, but unless more scientific methods are very widely adopted the time is rapidly approaching when it will be necessary to supply these products from another source, for present methods of operation are beginning to be looked upon as directly antagonistic to all ideas of conservation under American lumbering conditions, as they so weaken the trees that the loss from windfalls is extremely large. In fact, many large lumber companies have given up "boxing" for this reason, and also because they feel that the growth of the young tree is retarded.

Modifications of the old "boxing" methods are being used in some places. Metal cups are substituted for the box cut in the base of the tree and light chipping is being tried. It is claimed that the loss from windfalls is considerably reduced by some of these modern improvements. At least one large Southern lumber company is at present experimenting on 5,000 acre units in order to determine definitely, if possible, the merits of these new cups and other modifications as to yield and influence on windfalls, and also to decide the effect "boxing" may have on finished lumber.

### WOOD TURPENTINE

Wood Turpentine came into commercial notice about the year

<sup>1</sup> Presented at the 6th Annual Meeting of the Amer. Inst. of Chem. Eng., The Chemists' Club, New York, December 10-13, 1913.

1900. The name was, and is, applied to the product obtained from dead and down timber, a waste product called "lightwood." The live or green wood is not so suitable for this manufacture, owing to the moisture content and also to the fact that the bark still remains. Stumps, however, are very valuable, as they contain a much larger proportion of resins than "lightwood." Nevertheless, the cost per cord of stump wood is considerably more, as the stumps usually require the additional expense of removal by explosives. The cost per cord of "lightwood" at the works will run from \$2.00 to \$3.00, making, however, no allowance for its value as waste; while stump wood will vary from \$3.50 to \$5.00 per cord, the price depending on acre stumpage and hauling distances. The manufacture may be divided into five general processes; steam process, solvent process, alkali process, bath process and distillation process.

Before entering into a description of these various methods we desire to emphasize the statement that the manufacture of wood turpentine necessarily will become of far-reaching importance in the future. This is for the reasons that it is utilizing an absolutely waste product and is at the same time clearing cut-over lands and rendering them fit for occupancy. We wish also to emphasize the statement already made that many past failures were due to the unreasonable speculative condition of the markets. Abnormally high prices of naval stores induced promoters and unscrupulous persons to capitalize their concerns on the earning capacity during this period, thereby making them "stock jobbing" propositions rather than legitimate manufacturing institutions. This kind of financing while apparently expanding the industry really retarded development, as the energies of the management were expended primarily in the office and at the expense of the manufacturing organization.

We have seen from time to time figures of promoters, regarding yields and manufacturing costs of the different processes, which are not in accord with the results obtained from continuous operations. It may not be entirely without value therefore to cite some comparative yields and operation costs in these different processes, especially since there does not appear to be any published data of this nature. While the records themselves of individual plants would be interesting, such records are often misleading and in view of actual or possible competition, the location of plants must be withheld.

In submitting data as to yields, values and productive costs, we have compiled them mainly from the actual results obtained during continued operation of a number of large plants. As so many elements making up these figures are variable, owing to location, construction and raw material, our endeavor has been to average them so that a comprehensive idea may be had as to actual results obtained commercially.

#### STEAM PROCESS

This process was the first to be extensively placed in commercial operation, and is very simple in its construction and handling. It consists merely of "hogging" the wood and placing it in a steel cylinder, holding usually about a cord, distillation being carried on with live steam and under varying pressure. However, there probably was little difference in results whether a maximum of five pounds or twenty pounds pressure was used. Distillation was carried forward until oils ceased to be obtained in quantity.

It should be borne in mind that there is a decided variance in the resinous content of wood; therefore, it was quite possible to make a selection that would run as high as 30 gallons of turpentine to the cord. We believe the following figures, however, based on a cord of long leaf yellow pine lightwood, weighing 3500 pounds, would be the average.

The fuel cost is only the labor of handling the treated chips. However, there is no allowance made for the office, upkeep, depreciation, insurance, etc. Therefore, it can be seen that the steam process, in order to be profitable, necessarily demands

a market price considerably in advance of the present markets.

The price of Wood Turpentine is always a few cents per gallon under that of Gum Turpentine. The quality of the product

Turpentine	91/2 gals. at 35 cents	\$3.32
Pine Oil	3 gals. at 35 cents	1.05
Total value of products		\$4.37
Production Cost Per Cord		
Wood		\$3.00
Labor		1.00
Barrels		0.42
Freight (approximate)		0.20
Selling Commission		0.25
		\$4.87

produced by the steam process, however, is excellent. Our opinion is, nevertheless, that at least 50 cents per gallon is necessary as a minimum for successful operation.

#### SOLVENT PROCESS

In the early development of this process the wood was subjected to the old steam treatment and subsequently treated with carbon disulfide for the recovery of rosin. The loss of solvent rendered it impractical. In the next stage of development the wood was hogged and placed in digestors for the recovery of turpentine and pine oil. Then the solvent (a low grade of gasoline) was added, live steam was applied recovering some turpentine, pine oil, and solvent by distillation and the dissolved rosin drawn off, its volatile matter being recovered by distillation. This has been improved, in some instances, by omitting preliminary steaming, adding solvent direct and recovering this with the turpentine and pine oil by live steam in the primary distillation, obtaining rosin alone when the still is drawn. The rosin, however, is soft, and difficulty has been experienced in obtaining a hard product, but this is overcome by subsequent treatment. In either method a considerable loss of solvent is always entailed, varying from 17 to 30 gallons per cord. The approximate yields and operating costs per cord are as follows:

Turpentine—91/2 gals. at 35 cents	\$3.32
Rosin—400 lbs. at \$4.00 per 280 lbs.	5.72
Pine Oil—3 gals. at 35 cents	1.05
	\$10.09
Production Costs per Cord	
Wood	\$3.00
Labor	2.50
Loss in solvent at 15 cents (17 gals.)	2.55
Barrels	.42
Rosin Barrels	.25
Selling Costs	.50
Freight	.75
Total	\$9.97

Again the actual fuel cost in this process is negligible as use is made of the "treated chips." No allowance is made here for insurance, upkeep, overhead and interest charges, refining costs or depreciation; therefore, it is plainly evident that, at present market prices, at least until improvement is made in yields or in minimizing costs, there is not sufficient margin for successful operation. However, it is quite possible that by using the "treated chips" for paper pulp manufacture this process can be made of commercial value. The operation in this case would have to be maintained on an enormous scale in order to supply treated chips for a pulp plant unit of an economic size. A plant using this solvent system and built on a very elaborate scale, was in operation in southeastern Georgia, and, despite the most advantageous financial backing, was unable to operate profitably on a weakened market, and is now in the hands of receivers. This citation alone probably would not necessarily condemn the process, but as several smaller plants are either in like position or shut down, it indicates the necessity of research or development if ultimate success is to be attained. As with the steam

process, many claims of higher yields than we have above credited are made by interested parties, but these claims are still subject to substantiation.

#### ALKALI PROCESS

This process is essentially one to be applied to the alkali processes for manufacturing paper pulp from resinous woods with the recovery of turpentine and rosin and at the same time improving the quality of the pulp, and promoting ease of manufacture. The process is well covered by patents.

The basis upon which this method rests is the fact that the sodium hydroxide saponifies the resins in the wood and the sodium resinate thus formed may be separated from the spent soda pulp liquor by temperature regulation. The wood is handled in the same manner as in soda pulp manufacture, except that after digestion the spent liquor is cooled for the separation of sodium resinate before the liquor proceeds to the evaporators. This product has been so purified and refined, commercially, as to produce a good quality of paper size. The resinate may if desired be manufactured into resin by acid treatment, or destructively distilled to produce rosin oils. The turpentine is recovered from the digester blow-off during the digestion operation. This process is apparently theoretically sound, but requires the outlay of capital to develop thoroughly the mechanical details. Fifty to seventy thousand dollars were expended in one case to demonstrate its commercial possibilities and some results were obtained. However, the enterprise has not been financially successful and the plant has been dismantled, a fact which may be due to faulty engineering or other causes; and even though the process appears enticing from a theoretical viewpoint the fact remains that the trial was not successful and there is no process of this kind in actual operation. Nevertheless, it is our opinion that eventually it will be of commercial importance and ultimately the combination of the two industries, paper pulp and turpentine-rosin recovery, thus utilizing resinous wood, will be successful. Unusual yields of turpentine are claimed by a Florida plant using an alkali bath but satisfactory arrangements have not yet been made regarding rosin recovery.

#### BATH PROCESS

This process must not be confounded with the recently suggested process using a bath or envelope of oil external to the oven for the purpose of heating the same. This external bath process has not been long enough in operation to demonstrate its future and it will be interesting to note whether certain fundamental operation difficulties can be overcome.

By Bath Process we refer to the process commercially so called which has been in operation for some time and in which the bath is *within the oven* or retort in contact with the wood itself. Three plants using this method have been built, the first in North Carolina, which has been dismantled, the others at Mt. Pleasant, Georgia, and Jacksonville, Florida, which have not been successful owing to low market conditions and both of which have gone into receivers' hands within the last few months.

The process itself was divided into two separate general operations: first, the recovery of turpentine and pine oil, or "sweet spirits," and subsequently the destructive distillation of the wood itself, although this second operation was not contemplated in the original process.

The operation has a decided advantage over the solvent and steam processes in that it does not require the "hogging" of the wood.

The general construction used in this first operation consists of steel cylinders at Mt. Pleasant, and concrete ovens at the Jacksonville plant, each holding five to nine, one or two cord steel cars, similar in construction to those in common use in hard wood distillation; thus each oven holds about nine cords of wood. Placed at the side of the oven is a heater equipped with a large cast iron worm joined to the bottom of the oven. To the rear of the heater is placed a large steel or concrete reservoir connected by cast iron pipe with the top of the oven, and also with

rotary pumps which in turn are joined to the heater pipes.

The loaded cars are placed in the oven and melted rosin or pitch is run into the reservoir and circulated by the pumps through the heater and the bottom oven connection. This pitch after filling the oven *in contact with the wood* overflows into the reservoir and is thus continually circulated through the heater and oven, thereby vaporizing the volatile resinous bodies, without dissociating the wood fiber. The turpentine and oil vapors are carried through a "vapor" chamber in which the high boiling liquids that are mechanically carried by the vapor are separated, the vapor continuing to an ordinary tubular condenser, where the crude "sweet spirits" are obtained. Afterwards the "sweet spirits" are refined, the products being turpentine, pine oil and a tarry residue. The time required to treat a charge varies in the plants mentioned from seven to ten hours, and the product obtained is of high quality, though not so good as steam process turpentine.

At first sight it would appear that in this process the rosin from the wood treated would gradually increase the volume of the bath and rosin be thus manufactured. The reverse of this, however, is the case, as a serious loss of bath is actually realized. This is in fact a very serious drawback to the process, and is probably due to the formation of volatile rosin oils when the liquid bath encounters the high temperature of the heater. These rosin oils are volatilized and pass into the "crude spirits," and are lost in the refining residue, as only from 65 to 70 per cent of the spirits is received as turpentine and pine oil. By proper arrangement this difficulty could be avoided.

This process is also seriously handicapped by the fuel consumption of the heaters and the heavy upkeep for heater pipes and pumps. Nevertheless, with proper design, operation costs would be much reduced from that actually experienced.

After refining, the results from this "sweet process" could be averaged as follows:

Turpentine, 7 1/2 gals. at 35 cents	\$2.62
Pine Oil, 2 1/2 gals. at 35 cents	87
	\$3.49

After the charge is withdrawn in this first operation the "treated" wood is placed in ovens similar to those used in the hard wood industry and there subjected to destructive distillation. The results obtained here are very important as a good market has been created for these products. An average of from 68 to 70 gallons of oils is obtained, together with a like volume of "acid water," the latter a "waste," although its utilization was accomplished just prior to the receivership of one of the mentioned companies. In addition there remains in the cars approximately 900 pounds of charcoal and there is produced about 10,000 feet of non-condensable gas per cord which is of fuel value.

This crude distillate above mentioned is called "destructive distillate" or "D. D. Product" to distinguish it from the product derived from the resins, called "sweet spirits." On refining there are obtained the following products per cord:

Tar, 41 gals. at \$.08	\$3.28
Light Oil, 6.8 gals. at \$.12	.81
Heavy Oil, 10 gals. at \$.12	1.20
Charcoal, 36 bushels at \$.075	2.70
From "sweet process"	3.49
<b>Total</b>	<b>\$11.48</b>
<b>Costs of Production per Cord</b>	
Wood	\$ 3.00
Fuel	3.25
Labor	2.75
Cooperation	1.00
Selling Costs	.60
Freights (approximate)	.75
	<b>\$11.35</b>

Again it can be seen that this process handled as it has been



in the past cannot be operated successfully on a low market, as no allowances have been made for upkeep, insurance, interest charges, refining costs, management or depreciation. Although the loss in bath is partially made up by the pitch obtained, it can be seen from these costs that improvement must be had before this process can exist during low market conditions. It is not to be inferred, however, that the principles upon which the process is based are entirely faulty. The reasons for its failure appeared to be lack of knowledge as to the chemical nature of the products and troubles consequent to improper construction and operation. As is common with approaching dissolution strenuous efforts at improvements were made in this process, and despite well known prior failures, experiments were completed and operation commenced for the utilization of the waste "acid water" just before the closing of one of the plants. The results proved interesting and promised excellent recovery, as the products recovered, including acetate of lime and wood alcohol, represented a net gain of well over \$1.50 per cord.

#### DISTILLATION PROCESS

As the wood turpentine industry now stands, the destructive distillation process apparently has the best chance of commercial success, as it is not only more simple in construction and operation, but yields more in volume of products. Chemical and engineering skill, nevertheless, are necessary for this success.

The distillation process may be subdivided into three divisions: first, that division analogous to hard wood distillation. This method in its primary operation is very similar in equipment and design to the usual hard wood distillation plant, the wood being placed in steel cars and run into ovens. The products derived from the resins and those from the dissociated wood are collected together, and separation is made during refining, although some attempt has been made at fractional distillation in this primary stage. This method gives a much inferior grade of turpentine, etc., owing to the commercial difficulty of eliminating the pyro-ligneous bodies, and the product will not answer to the per-man-ganate test which indicates pyro-ligneous matter. The tar produced in this operation is usually resinous and for some uses, therefore, objectionable.

The second division is merely a modification of this process, the ovens being in duplicate, and distillation for the resinous bodies being carried out in one oven, so designed or "set" that the temperature can be maintained approximately uniform. After the resinous bodies have been obtained the "treated wood" is withdrawn and placed in a second oven and in this oven the distillation is carried at a higher temperature for the destructive distillation of the wood itself.

The third division is that using concrete ovens containing 12 inch heater pipes running the length of the ovens. These ovens have duct-oven connections and the flue gases travel through these pipes, and it is claimed that temperature regulation is more easily accomplished.

In all these processes the products obtained are the same, except so far as the degree of purity is concerned.

The first distillate, or that from the resins in these methods, will run on an average 22 to 24 gallons of "sweet spirits." This on refining will give from 50 to 60 per cent or from 12 to 14 gallons of marketable turpentine and from 9 to 10 per cent or from 2 to 2½ gallons of pine oil, and also 100 pounds of a very resinous pitch.

The destructive products are the same as those from the "bath process;" thus it can be seen that the gross total in this operation should be materially higher than in the other processes, while the operating expense is very much lower. This, including wood, upkeep, and in fact all expense, should not, under proper design, construction and management, run over \$9.00 a cord.

The particular objection raised against the destructive distillation process is that the products are difficult to market, and

this has been true to a certain extent in the past, but when it is considered that many of these products were new to the trade this condition cannot be wondered at, and at present the marketing is not more difficult than products of other processes. In fact, just now there is an unusual demand for these products.

#### MARKETS

It may, perhaps, be of interest to call attention to the various developed markets for the D. D. Products, for we all realize that the marketing of products is at least equal in importance to the manufacture; and this industry shows many instances where comparative merit of process and operation was wholly lost by inferior marketing facilities, and, on the other hand, instances in which unsound operation was maintained for a considerable time by a remarkably efficient selling organization. The latter cases, while losing ventures to those financially interested, have no doubt succeeded in creating a growing demand for the products, as indicated by the prices now obtained for them, with many plants closed down. At the present time tar could be easily sold for 12 cents per gallon as compared with the 8 cents allowed in the cost data in this article, but which should be considered maximum, as the future will undoubtedly increase supplies so as to bring these prices back to a more nearly normal condition. This fact, however, does show that a demand has been created that did not exist prior to the quite recent establishment of plants of this nature. Perhaps this condition is more clearly evidenced in the heavy D. D. oil, for which 22 cents per gallon is being obtained. The tar demand had in a measure been previously supplied by that known as "kiln tar" made at works using the kiln system for charcoal manufacture from resinous woods.

The product mentioned as D. D. light oil is at present most difficult to market profitably. It is on the market in this form and is used to some extent by manufacturers of disinfectants. However, it has been fractionally distilled and has been used locally as a substitute for gasoline for use in engines and has proven itself to be more efficient than gasoline. The comparatively small amount of this product makes its use in this manner merely of local interest but it indicates a real value of the product.

The heavy D. D. oil has been in consistent and increasing demand, particularly in the paint industry, and notably for shingle stains; also for the manufacture of tar oils for which there is a large foreign demand. The necessity of an energetic market agency for this product was in one case well illustrated within the past year. One large concern, having nearly 100,000 gallons in storage, and finding it impossible to market, was offering it for 5 cents per gallon, while at the same time another company was unable to supply its customers at 18 cents per gallon. Of course, the latter considered the purchase from the former, but feared future competition in case, as seemed dangerously probable, the former concern should learn of their customers.

The pitch produced in the distillation process and distinguished from the tar has a firm market demand from ship chandlers and also is sold for uses such as coating silos, rendering them impervious to moisture.

The tar, of course, has its established use with rope manufacturers as well as with paint producers, while the charcoal consumption, particularly in the south, is very steady both for domestic use and manufacturing. Of the number of suggested specialties based on the use of tars and oils, doubtless a few will ultimately contribute a steady demand for a portion of these products.

#### COSTS OF INSTALLATIONS

The various processes have in most instances exceeded reasonable installation costs. Undoubtedly the same is true in any newly established industry, and more particularly in cases where, as pointed out in this one, prices could be obtained that were out of all proportion to production costs.

The entire equipment of a steam process plant should come well within \$750.00 per cord capacity, while the solvent process complete should be approximately \$2,000.00 per cord. This also should be approximately that of the bath system, while the destructive distillation method ought to be very close to \$1500. In making these general estimates neither working capital nor purchase of timber or stumpage is considered.

#### CONCLUSION

When your attention is brought to the fact that the destructive distillation plants alone have been able to survive recent price depression, it is reasonable to conclude that, in the present state of the art, this method has inherent advantages. Nevertheless, in this type of process there is room for much improvement, particularly in refining and the utilization of waste products that were ignored in the past. Constructive chemical engineering in this industry apparently has opportunity to create an unusually profitable business, provided it utilizes the unfortunate mistakes of the past, by combining parts of the various processes.

It is not to be inferred from this article that recommendations are made for the encouragement of any particular process. The motive is merely to outline present conditions or, broadly, to show cause and effect; and also to show, if possible, that in order to attain success, many elements are as necessary in this industry as in any other. Statements have been made to the effect that failures in most instances were due to lack of real engineering skill, and this is partly true, but lack of skill is not wholly accountable for even the engineering failures, as no amount of theoretical engineering skill can replace the knowledge acquired from continued intimate contact with the going operation.

Neither does this statement take into consideration the marketing organization, which is also an essential, and is always confronted with the general economic situation, although this does not affect directly the operation.

It can be seen from this outline of the industry that its very existence was primarily due to an unnatural market condition, and as the field for profit and exploitation was so enormous it can hardly be wondered at that there was unusual activity in its promotion.

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### CHEMISTRY AS AFFECTING THE PROFITABLENESS OF INDUSTRY<sup>1</sup>

By G. W. THOMPSON

In the preparation of this paper I had thought of considering chemical industry as if it were distinct from other industries, but, as the subject developed, it became very apparent that no such distinct line could be drawn. Properly speaking, all industries must be considered as chemical. It is next to impossible to imagine the existence of an industry in which chemical reactions or considerations, either directly or indirectly, do not enter. It is possible that we could define chemical industry in a somewhat restricted sense, but such a definition would hardly be other than arbitrary. The lines of demarcation would be indistinct and shadowy. The only basis for such a definition would be the attitude of the popular mind. This attitude of mind has been steadily growing towards the recognition of the fact that chemistry is an important factor in every industry, and when, in any particular case, it becomes popularly recognized that chemistry is a factor in an industry, then that industry becomes a chemical industry. Ultimately, this popular recognition will extend to all industries and the rapidity of the growth of such recognition indicates that the time is not far distant when all industries will be generally and popularly recognized as chemical.

My plan had been to discuss the profitableness of chemical industry, but if we accept the conception that all industries are chemical, it would seem better that our discussion should be

<sup>1</sup> Chairman's Address before the New York Section of the Society of Chemical Industry, The Chemists' Club, October 24, 1913.

broadened so as to consider the general effect of chemistry upon the profitableness of industrial operations, using the words "industrial operations" as including all phases of the actual production of wealth.

Perhaps it would be well to make clear the conception that all industries are chemical in one or more phases. By way of illustration, let us consider the relation of chemistry to the production of power. I think we can show that there is a very close connection between chemistry and such production, and also that there is no industry which does not depend upon the consumption of power; this being the case, it becomes very evident that, from the power standpoint alone, all industries are chemical industries.

Our first impressions of power are those which we ourselves are conscious of exercising, and, in practice, the simplest form of power is man power as manifested in manual labor. It is not customary, perhaps, except from the humanitarian standpoint, to consider the chemical changes in the human body, converting food into work, as factors in industry. Nevertheless they deserve serious consideration. It is being learned daily that properly fed employees are more efficient as workmen, and the study of food problems is surely a phase of the application of chemistry to industry. In some industries, the study of the food consumed by employees has a direct bearing upon the health of the employees as affected by the industry. It is found that certain foods act as prophylactics towards certain industrial diseases, and that other foods (perhaps improperly so called) act in the opposite manner. The scientific study of foods in connection with efficient manual labor is a phase of welfare work that has not been considered to the extent it deserves. Take, on the other hand, the horse. It is true that the horse is being displaced by the locomotive and automobile, and as a power factor, has been almost completely superseded by mechanical appliances; still, so far as the horse is used for the power he furnishes, his proper feeding is a phase of the application of chemistry to industry. Perhaps it may be considered that these two illustrations, the feeding of employees and the feeding of horses, are trivial as compared with the study of the production of power through the use of the steam boiler, the steam engine, the gas producer, and the internal combustion engine. Probably this is so, for, in the production of power by these mechanical means, we have clearly recognized chemical reactions, and the understanding of these chemical reactions is essential to the proper economy of fuel and the production of power with the least outlay. In these cases, chemistry teaches us the need of a proper balancing of the combustible material used and the air supply, so that the loss of heat in effluent gases may be reduced to a minimum. In the steam boiler, chemistry has taught much of great value in relation to the refractory materials used, the utility of water consumed, and how to correct its scale-forming tendencies. In recent years, numerous excellent devices have been developed for automatically giving information as to the composition of flue gases, with the result that great savings in the cost of power have been made. The study of the composition of coals has resulted in a better classification of coals, a truer connection between price and quality, and the purchase of coals by specifications involving chemical examination is becoming more extensive each year. The small power plant cannot perhaps give as much attention to chemical factors as can a large plant, but in large power plants, the economy resulting from the study of the chemistry of combustion has enabled such plants to furnish power to outsiders with a profit to themselves and to those to whom they sell it. Chemical considerations led to the use of blast furnace gases in the gas engine for the production of power; and if the chemist's dream comes true, there will come a time when power will be more directly produced from coal than it is to-day. It is, of course, recognized that in the utilization of the energy in our



great waterfalls, chemistry is an unimportant factor, but here there is the compensating fact that many of our great chemical industries have been dependent for their existence and growth upon the cheap power thus produced.

This is as far as our time permits us to speak of the influence of chemistry upon the production of power. The scope of this paper will not allow a more detailed treatment of this subject, and what we have said is more as a matter of obvious illustration of one point of the dependence of the profitability of industry in general upon chemical factors; hence, we shall proceed to recount other phases of the relation of chemistry to industry.

The simplest phase is undoubtedly that relating to the purely commercial end of industry, wherein goods are bought and sold subject to analysis, the analysis being presumed to indicate the commercial value of the goods. These goods may be in the raw state, partially finished, or finished and ready for consumption. The oldest form of this kind of analytical control was undoubtedly for the valuation of precious metals and the ores containing them. The accuracy with which gold and silver can be determined by fire assay was recognized in the early stages of metallurgical development. The fire assay corresponded on a small scale to the actual recovery of gold and silver in smelting operations. It was natural, therefore, to assume that a similar correspondence existed between the fire assay of other metalliferous substances and the smelting operations then practised. What could be done with gold and silver, however, could not be done with the same accuracy with the more readily oxidized metals, and while the fire assay method is still applied in some places to metals other than gold and silver, in general, these processes have been superseded by wet methods, which are more obviously chemical in their character, and of greater accuracy.

The chemical testing of commodities sold under specifications is primarily for the purpose of protecting the purchaser, although accuracy of testing is necessary in order that justice may be done to the seller. Practically all raw materials dealt in in quantity are sold subject to chemical analysis. Chemical analysis may not be specified in the sale or made use of by the purchaser, but, in some form or other, the purchaser has the right to test out the products received, to see whether the terms of the sale have been lived up to. Very few commodities are sold to-day in regard to which there is not some recorded information on which a purchaser can base claims, if chemical analysis shows these commodities to be different from those described in the order or contract.

If we consider, however, the whole question of the purchase of commodities on either tacit or openly acknowledged chemical requirements, we shall see that chemistry has had a great influence in determining the profitability of industry, in preventing the delivery of inferior raw or semi-raw materials, which would ultimately affect the yield or quality of the finished product. The whole operation of our pure food and pure commodity laws depends upon the availability of chemical analysis and testing, and it is only natural that the rapid growth of sentiment in favor of these laws should have produced some commercial hardships which have led to the criticism of chemical control and standards as being too rigid and unsuited to popular requirements. Nevertheless, such pure commodity laws have been of great profit to the purchasing public.

But if chemistry has had a great influence upon the profitability of industry in the purchasing of commodities, what shall we say as to its effect on the profitability of industry in the sale of commodities? In the popular mind, profits are made on sales, not on purchases, and the salesman seems to be, to use the language of the streets, "the whole thing." Most businesses are dominated by the salesman, be he proprietor, manager, or drummer. According to this idea, in the making of profit, the salesman is a factor greater than the purchasing

agent, or even the manager of the manufacturing department, considering that these are distinct from each other. There is undoubtedly a great deal of truth in this conception and the popular idea rests on fairly well established facts. Taking this to be the case, what has been the influence of chemistry on the sale of commodities as affecting business profits? It is generally admitted that the old-fashioned personal influence of the salesman over the sale of his goods is growing less year by year. In place of this old-fashioned personal influence is coming a newer influence in which the salesman secures his sales, not by debauching the purchaser, but by his intelligence and the helpful knowledge which he possesses about the goods he sells, and, we must add, the confidence which the purchaser has in the salesman because of his possessing that knowledge. It is no longer the general practice to keep salesmen ignorant of processes of manufacture and use, but salesmen are being educated in many cases by technical men, often chemists, on the merits of their goods and how they may properly meet complaints. Then, too, the chemist's influence in improving the quality of products assists the salesman by giving him more salable products. I cannot take more than passing and regretful notice of the fact that there are some few chemists whose occupation appears to be mostly that of showing how goods may be debased without easy detection. The influence of the chemist in improving the quality of goods shows itself in the increased price which may be obtained for such goods. Perhaps, also, we should mention the general effect upon the commercial atmosphere of a business that has trained chemists in its employ, who give confidence to the general public that its products are made as well as possible with the assistance of the best that science can give.

With reference to actual manufacturing operations, we shall consider what the chemist has done in controlling manufacturing processes, correcting losses in manufacture, assisting in the invention of new methods and in the development of new uses for regular products, waste products, and by-products. Work along this line is particularly attractive to the chemist, and, in some cases, can be conducted profitably only by the chemist. The extent to which chemical knowledge is necessary or desirable can, of course, be determined only by considering each case by itself. There are, in all cases, practical limitations, in regard to which the chemist should be reasonable. Simply because, in general, chemistry is helpful, it must not, therefore, be assumed that in every case the chemist can increase the profitability of manufacturing operations, because it must be remembered that the chemist is worthy of his hire, and that hire may more than absorb the value of what he may accomplish. In the control of manufacturing processes, if uniformity of product is desired, there is probably no one better qualified than the chemist to establish such control. This he will accomplish by the systematic study of all the materials entering into the process and the product in all stages of manufacture, discovering the chemical reactions of the process, where these reactions occur, and how they can be accelerated to advantage or made more complete, if that is desirable. Considering in the abstract the manufacturing operation involving a consumption of raw materials, heat, power, and labor, the fundamental units of cost are the time consumed and the quantity of product made. The chemist should possess an analytical mind, and, in the study of a manufacturing process, he will endeavor to develop the effect of these fundamental factors and seek to control the other cost factors, keeping in mind the preservation of the full value of the chemical reactions taking place. Chemistry has been a great help and profit to industry in the control of manufacturing losses, and the business man who fails to recognize its value cannot be considered as practical. For the avoidance of such losses, the chemist is peculiarly fitted. Some industries, it is true, can be conducted profitably with large losses of some of the constituents contained in the raw materials, but, in the course of time, these



losses must be controlled, for the industry that applies the best control will be the most profitable and the best able to withstand competition. This can be done only by systematic chemical examination of the materials used and by systematic study of the chemical reactions entering into the processes. But the work that chemistry does in preventing losses in manufacture is not merely the direct prevention of such losses. Chemistry impresses itself sooner or later upon the manufacturer if he is awake, even though he be not technically trained, and he realizes that his manufacturing operations are not shrouded in mystery. The question of yield comes under the law of the conservation of matter. Matter does not disappear without going somewhere, and if it does disappear, it has been stolen, or some mistake has been made in accounting, or the matter has been changed in form, or actually lost in some of the refuse products. This is an exceedingly important subject. Many untechnical men think that yield, as they would express it, is "purely a practical question" and that losses in manufacture, like taxes and death, are something that we cannot get away from. The chemist valiantly attacks this belief. He asserts that losses occur for material reasons. This attitude of the chemist is simply a rational attitude which increases very materially the profitability of industry. In developing new uses for regular products, waste products, and by-products, the chemist has left his indelible mark upon industry. Here, he is in the lead, and his constructive mind is not satisfied with announcing his immediate discoveries, but in pointing the way to the rich fields of possible discovery that lie before him.

It is proper here to elaborate a little on the value of chemical societies and their journals. Chemical societies, seeking at all times to bring out the most recent information bearing on chemical problems, obtain numerous papers, which, published in their journals, are available, in most of our large public libraries, to business men whether technically educated or not. Frequently, the information which they may want is obtained in complete form in these journals. In other cases, the information has to be interpreted by chemists, and in still other cases, the information is so distantly connected with the problems involved as to be available only to chemists who open up vast possibilities of profit to industry. It is hardly to be expected that the chemist will be acquainted with all the published facts relating to any problem, but if he knows where these facts may be obtained, and if he knows how to interpret them, they soon become available, no matter how long they may have remained buried in the literature of the subject. The application of such facts frequently develops new ones, which in their turn may have high potential value. So valuable are these chemical records that I must not lose this opportunity of pointing to the great service chemists are doing and to urge them to enlarge this service to the greatest practicable degree by further contributions. The knowledge which we may possess is of value to us individually, but in the general service of mankind, we can frequently impart some of this knowledge, without hurting ourselves, at the same time extending a helping hand to others.

Much has been written upon the influence of the research chemical laboratory on the profitability of industry. Valuable information is on record showing how, in numerous cases, the research laboratory has been a tremendous profit to industry. In some cases, the research laboratory is devoted almost entirely to the development of new processes and products, and it would appear that the Germans have most successfully applied this method, and that their commercial high standing in chemical manufacture has been more due to this than to any superiority in methods or economies in manufacturing. While this is true, it appears to the writer that the research laboratory has another function not usually recognized. If I were to try to define this function of the research laboratory in popular language, I would say that it keeps the industry "ahead in the game."

It is not only in the concrete things which the research laboratory does that its profitability is to be measured, but its real value is also in the general advance work that it does. It gives to an industry a proper understanding of the needs of the trade. The industry that does not keep itself informed as to these needs is sure to lag behind. The fundamental information as to the needs of the trade can be furnished only by the chemist who has studied the possibilities, theoretical and practical, of both processes and products. The research laboratory is destroying trade superstitions which have hindered progress. It has furnished information to salesmen which they have been able to use to practical advantage. It has been in many respects the reflective organ of industry. The research laboratory could not have been any of these things if it were not continuously studying the problems presented directly and indirectly to it and availing itself of the invaluable records preserved in our chemical journals.

In those industries involving the manufacture of chemicals or in which chemistry is a predominating and obvious influence, the chemist is, of course, appreciated, although there are many such industries which do not utilize the chemist as fully and as completely as would be to their advantage. The really successful and profitable chemical manufacturing industries avail themselves of the services of the best chemists obtainable.

The indirect influence of chemistry upon the profitability of industry should not be overlooked. The philosopher who once said something to the effect that the man who made two blades of grass to grow where only one grew before is a public benefactor, stated a truth that applies with a special force to the chemist. The discoveries of chemistry which have been of no direct value to the discoverer, but have been of great indirect value to humanity, are innumerable. Sometimes a chemist is looked upon with scorn because he has not made personal profit out of his discoveries, which he has published to the world and made common property. This form of communism is idealistic. The discoveries of Pasteur have added immense profit to the fermentation industries and have been the saving of innumerable lives. I know of no class which contributes, as chemists do, so freely to the fund of general knowledge on which profitable business is based. Then too, there is the indirect saving which the chemist is responsible for in the conservation and utilization of industrial products. The studies relating to the corrosion of iron and steel and indeed to all of the phenomena of decay have resulted in greater permanence and durability of the products of industry, the benefits of which all industries may share.

In arguing, as we have, in favor of the proposition that chemistry is a powerful factor in making industry profitable, we must not close our eyes to its limitations. The chemist should be a business man in the best sense of the words, and should recognize that in all successful business operations a proper balancing and coordination of all its factors is necessary. The study of power problems should be made, but the extent to which expenditure for the study of power factors should be made depends upon the importance of the power factor. The testing of materials purchased and used should be made, but the extent to which such testing should be made can be determined only by the proper consideration of its relative importance. New processes and products should be developed, but there is a limit to expenditure for these ends, which limit is in the hope of profit to be derived. After all, all industry depends upon the production or exchange of articles that are desirable, and the desirability of an article is a determining factor in its value. But not merely must a product be desirable, it must be produced with proper economy, for that is a limiting factor affecting its marketability.

We have discussed this subject in an abstract manner. Many illustrations could have been introduced of how industries have

profited through the assistance of chemistry. We have thought it better, however, to omit such illustrations, but hope that during the coming year we shall have many papers practically demonstrating that what we have presented in the abstract is concretely true. When we speak of chemistry as affecting the profitability of industry, we must bear in mind that, while all chemical knowledge may be said to come from the chemist, such knowledge is often made use of with profit by those who are not chemists. This is something that is unavoidable, and it seems to me no attempt should be made to make it avoidable. The benefits which chemists derive from the more general diffusion of chemical knowledge are very much greater than would be the case if chemists were successful in an attempt to

make their profession esoteric. The progress of humanity cannot be accomplished by making the study of chemistry and the benefits that come from it profitable only to the chemist. It is proper that the chemist should seek to obtain profit from his knowledge and ability, but he cannot hope to do this except in some few cases, unless he is willing to give to others at least a portion of the knowledge that he possesses. All industries and occupations are interdependent. All industry depends upon the chemist and the chemist depends upon all industry. The more this interdependence is recognized, the greater the profit accruing to industry, and the greater the return to the chemist.

129 YORK ST., BROOKLYN

## PERKIN MEDAL AWARD

The Perkin Medal was conferred on John Wesley Hyatt for his distinguished services in the field of applied chemistry and engineering at the regular meeting of the New York Section of the Society of Chemical Industry, held at The Chemists' Club, on January 23, 1914.

The meeting was opened with an address by Dr. G. W. Thompson, Chairman of the Section, and the presentation address was made by Professor Chas. F. Chandler, Senior American Past-President of the Society of Chemical Industry. The acceptance by Mr. Hyatt was followed by an address by Dr. Frank Vanderpoel.

The inventive genius of the medalist together with an intimate description of the history of his developments was ably treated by the various speakers, and the addresses are printed in full in the following pages. [EDITOR.]

### CHAIRMAN'S ADDRESS

By GUSTAVE W. THOMPSON

At this meeting of the New York Section of the Society of Chemical Industry, it becomes the pleasant duty, through established methods, to award the Perkin medal to the person selected as most worthy for valuable work done in applied chemistry. It seems hardly necessary that a statement be made as to the origin and history of the annual presentation of this medal further than to say that the medal was founded in commemoration of the fiftieth anniversary of the coal tar color industry, the cornerstone of which was work done by the man whose name is attached to the medal. There are, however, certain features which are forced upon our attention annually in the selection of the person to whom this medal should be awarded, which it may be desirable to consider in opening this meeting.

As stated above, the medal is awarded for valuable work in applied chemistry. Whatever the future may have as interpreting the grounds for merit, in the past it has generally been considered that this work should be in the nature of original or inventive work which has proved of great public value. The questions I would propound to you to-night are: What is the mental faculty which has made the recipients of the Perkin medal what they are? In what respect, which has enabled them to be so successful in the application of chemistry to the arts, do these men differ from their fellow chemists? I have given considerable thought to these questions, and I wish to submit my conclusions for your consideration, believing that they may be of some suggestive value.

In 1870, Tyndall delivered his famous discourse on the "Scientific Use of the Imagination." In this discourse, he showed the value of the imagination properly made use of in solving some of the most difficult problems of physics. Tyndall has shown us how the imaginative mind, seeing resemblances in things, can supply the missing parts in such resemblances, those missing parts being hidden from the senses. It was this power of the imagination which enabled Kekulé to form the

basis for the working out of the structure of many complex organic compounds; that work has been of incalculable benefit to chemical science and industry. Thousands of instances could be given showing that practically all of the progress made in the science of chemistry has been due to this proper use of the imagination.

Considering the work done in applied chemistry, we see clearly that it was the imagination of Herreshoff that enabled him to develop the metallurgy of copper; and of Behr in his work on the separation of the oil contained in the germs of corn; and of Acheson, who saw in his imagination that, if flocculating agents existed, there were probably also *de*-flocculating agents; and of Hall, who believed that somewhere there was a solvent for alumina from which aluminum could be obtained electrolytically; and of Frasch, who saw in the oil and salt wells the suggestion of the possibility of recovering sulfur from the bowels of the earth; and of Gayley, who saw the possibility of the dry blast in increasing the output and decreasing the cost of the blast furnace; and ——— of Hyatt, who saw in the drop of dried collodion the possibility of producing a plastic mass, which was finally obtained in celluloid.

It was Tyndall who emphasized the extreme value of the two little words "as if" when used by the scientific mind, showing how, from things seen, a scientific imagination can lay bare things unseen and make possible discoveries of great value. Discoveries often come by accident, but it is the imaginative mind that sees in these discoveries future possibilities. It is the imaginative mind which, following our discoveries so made, is led into unlimited fields of usefulness. We must not think, however, of imagination as being the sole factor, although it is probably the principal factor, in the production of valuable materials. There must be energy, concentration, and persistence, which will carry such a mind across the Jordan into the promised land. Nevertheless, the imagination is the most important factor here, because, without it, there would be no promised land.

As we look around about us upon those with whom we are intimate, we see this imaginative faculty in all degrees of development, and I have this word of suggestion to offer—those of us here who are educators, in whose hands are being moulded the minds of future chemists—should we not ask them whether the work which they are doing tends to develop this imaginative faculty, or whether it is indeed possible for them to sow in the minds of their students the seeds of imagination if they do not already exist there? It seems to me that there is no better place, no better occasion, than this place and this occasion, when we are honoring, by the presentation of the Perkin medal, a man in whom the imaginative faculty was highly developed, to put before you the need of the imaginative faculty in as emphatic a manner as possible and to urge that in our educational institutions this faculty should be developed to the highest de-

gree. For, if we are honoring Mr. Hyatt on account of his possession of this faculty, should we not seek to increase the number of those who possess the faculty in a high degree? Is not the real purpose of the Perkin medal something more than the honoring of its recipients—great as that purpose is—is it not all done for the purpose of encouraging those faculties on which the presentation of this medal rests?

### PRESENTATION ADDRESS

By CHARLES F. CHANDLER

MR. CHAIRMAN, DISTINGUISHED GUEST AND BROTHER CHEMISTS:

It is my very pleasant privilege as the senior Past-President of the Society of Chemical Industry, residing in this country, to present to John Wesley Hyatt the eighth impression of the Perkin gold medal, in recognition of his most valuable work in applied chemistry.

Mr. Hyatt was born at Starkey, Yates County, New York, in November, 1837. He was educated in the public school and later in the Eddytown Seminary where he excelled in mathematics.

In his early boyhood he acquired a strong taste for mechanical affairs in his father's blacksmith shop. In his sixteenth year he went to Illinois and learned the printing business, working at this trade for the following ten years. During this period he made his first invention, a family knife sharpener which included a new method for making solid emery wheels.

He then went to Albany and worked as a journeyman printer for about two years. Seeing a \$10,000 offer for a substitute for ivory for billiard balls by Phelan & Collander of New York, he began experimenting nights and Sundays in the hope of gaining the reward. He made a number of useful plastic compositions, none of them however good enough for billiard balls, but he started to make checkers and dominoes of pressed wood and with his two brothers established in Albany, New York, what is now the Embossing Company which has been a highly successful concern for more than 40 years, under the mechanical management of Mr. Hyatt's younger brother, C. M. Hyatt.

In 1870 he invented and patented a machine for turning billiard balls, by which an unskilled workman can do as much as a dozen skilled workmen could accomplish by former methods, securing at the same time perfect accuracy.

His attention having been called to the character of the solid nitrocellulose left by the evaporation of liquid collodion, or artificial skin as it was called when collodion was first put upon the market, for covering cuts and other wounds, he turned his attention to the subject of nitrocellulose as a suitable material for producing plastics. It should be remembered that gun cotton or nitrocellulose was first discovered by Schoenbein in 1845. In 1847 Maynard announced the discovery that while nitrocellulose is not soluble either in alcohol or ether alone, it is soluble in a mixture of the two and he gave the name collodion to the solution, which has since found its way very extensively into medical use. It also served to solve the problem of producing photographic pictures, either positives or negatives, upon glass, practically sounding a death knell for the beautiful though expensive daguerreotype process. The wet collodion process was introduced by Scott Archer in 1851.

Hyatt was entirely ignorant of the various efforts which had been made by Parks, Spill and others to utilize soluble nitrocellulose or pyroxyline for the manufacture of plastic materials, and consequently he started out without any hints or suggestions as to how he should proceed. His first success resulted in the manufacture of billiard balls by first making a solid core of another plastic material and covering the same with nitrocellulose dissolved usually in ether and alcohol. The process was so successful that a good business was established in 1870 which continued for several years.

In the meantime Hyatt invented celluloid and began the manufacture of celluloid and bone dust billiard and pool balls. At this time his brother, Isaiah S. Hyatt, joined him and they worked together until the brother died in March, 1885.

I do not propose to give a detailed history of the progress made by Mr. Hyatt and his brother in establishing the celluloid industry. I shall merely remark that Hyatt's patent 88,633, dated April 6, 1869, was for a molding composition to imitate ivory and other substances composed of fibrous material and gum shellac or other solid fusible adhesive gum. His patent No. 88,634, dated April 6, 1869, was for an improved method of coating billiard balls, consisting in dipping the billiard balls made of some suitable composition into a solution of collodion which might be given any desired color beforehand. His



JOHN WESLEY HYATT, PERKIN MEDALIST, 1914



patent 89,582, dated May 4, 1869, was for a composition consisting of ivory dust or its equivalent mixed with collodion and subjected to pressure during the evaporation of the solvent. Patent 91,341, dated June 15, 1869, taken out by the two brothers jointly, was for manufacturing solid collodion with very small quantities of the solvent dissolving the pyroxyline under heavy pressure, thus securing great economy of solvents and a saving of time.

Their patent 105,338, dated July 12, 1870, shows the fundamental invention of celluloid. It is entitled "Improvement in Treating and Molding Pyroxyline." The three claims of the original patent are:

1. Grinding pyroxyline into a pulp, as and for the purpose described.

2. The use of finely comminuted camphor-gum mixed with pyroxyline pulp, and rendered a solvent thereof by the application of heat, substantially as described.

3. In conjunction with such use of camphor-gum, the employment of pressure, and continuing the same until the mold and contents are cooled, substantially as described.

This patent was reissued three times in order to avoid ambiguities. The claims of the last reissue are as follows:

1. The use of finely-communited camphor-gum mixed with pyroxyline pulp, and rendered a solvent thereof by the application of heat, substantially as described.

2. In conjunction with such use of camphor-gum, the employment of pressure, and continuing the same until the mold and contents are cooled, substantially as described.

The specification fixes the proportions at about 1 part of camphor to 2 parts of pyroxyline. Modifications of this process were embodied later in U. S. Patents 156,352 and 156,353.

From this time on celluloid became a most important plastic, superior in almost every respect to any other plastic hitherto proposed, for the manufacture of the greatest variety of articles, useful and ornamental.

Seventy-five different patents were taken out either by John Wesley Hyatt alone or in association with his brother Isaiah S. Hyatt, and an enormous establishment grew up at Newark in the hands of the Celluloid Company.

I should not take up your time by enlarging further on the history of celluloid were it not that in one of our most important and most recent works on applied chemistry, I find it stated as follows under the head of celluloid:

"The substance was first produced by Daniel Spill of Hackney, England, and come into commerce under the name of 'Xylonite.' Spill's method of converting the nitrocellulose has been followed for more than forty years."

I have had occasion, in connection with celluloid and nitrocellulose litigation, to study most carefully the history of the pyroxyline industry and there is no logical ground for making the above statement. Celluloid was invented by the brothers Hyatt, and not by anyone else. This whole matter has been thrashed out in the Federal Courts as long ago as 1886, and the Hyatt patents have been sustained although everything that had been patented or published was carefully studied and discussed during the litigation.

It is quite true that many other experimenters sought to prepare useful plastic compounds with the aid of pyroxyline prior to the Hyatt invention of celluloid. Most prominent among these experimenters, we find Alexander Parks and Daniel Spill but neither one of them ever suggests the essential features of the Hyatt method for manufacturing celluloid. Parks' patents relate to the following points: (1) Making liquid solutions by the use of various solvents, rendering the material less inflammable by adding chloride of zinc or tungstate of soda or gelatine dissolved in acetic acid. (2) Making sheets by pouring the solution on glass and allowing it to evaporate. (3) Dehydrating wood alcohol or naphtha as a solvent by distilling

over chloride of calcium. (4) Adding castor or cottonseed oil, gums or resins or oil previously treated with chloride of sulfur to his solvents. (5) Introducing nitrobenzene or glacial acetic acid or hydrocarbon solvents. In one patent he proposed to remove the solvent from the solution of pyroxyline by adding water, mineral naphtha or other liquids. In another patent he gives compositions to be used as a varnish. There is nothing whatever in any one of these patents that anticipates Hyatt.

As for Daniel Spill, his patent 2666 of 1867 (English) suggests as substitutes for dehydrating alcohol or wood naphtha as a solvent for pyroxyline: fish, vegetable oils, essential oils, resins, gum resins, spirits of turpentine, fats, light oils and naphtha from coal and mineral naphthas. One example of a suitable solvent contains 80 per cent alcohol and 20 per cent of rosin. Another contains 60 per cent of alcohol, 3 of castor oil, 1 of essential oil of lavender, 3 of resin and 34 of coal naphtha or benzole.

The Spill patent 3984 of 1868 claims the production of compounds of "Xyloidine" by the employment of nonvolatile solvents, mentioning animal, fish, vegetable, or mineral oils, as mineral tar, lard oil, cod liver oil, camphor oil or liquid camphor, linseed oil or heavy coal oils or mixtures of the same. He further states that the following substances may be added: paraffine, camphor, resins, fat, wax, india rubber, gutta percha or balata gum or mixtures of the same. He gives the following example:

Camphor, camphor oil, or liquid camphor.....	20 parts by weight
Oil, such for example as castor or linseed oil, either before or after such oils have oxidized or boiled....	40 parts by weight
Xyloidine.....	40 parts by weight

The claim of the patent is for the production of compounds of Xyloidine by the employment of nonvolatile solvents. This is also the essential feature of the claims of Spill's American patents 91,377 and 91,378 in 1869.

Spill took out another British patent 3,102 of 1869, substantially identical with U. S. Patent 97,454 of the same year. This does not differ materially from his prior patents. He mentions a great variety of solvents, many of them given in his previous patents and these he groups under eight numbered paragraphs and gives the following as the only example of his invention:

Xyloidine.....	27 parts by weight
Castor oil.....	27 " "
Camphor.....	6 " "
Solvents, either of the Nos. 1, 2, 3, 4, 5, 6, 7, 8.....	40 " "

The Spill patent 180 of 1870 is for bleaching Xyloidine. His patent 787 of 1870 and his U. S. patent 101,175 of 1870 are for the employment of evaporating and concentrating apparatus, to remove the solvent from the fluid preparations and convert them into masses of a greater degree of consistency, at the same time recovering the volatile solvents evaporated.

These inventions give a fair picture of the condition of the efforts to make a useful plastic from pyroxyline prior to the date of Hyatt's invention of celluloid which was patented July 12, 1870, and which in the clearest and most unequivocal language sets forth the nature of his invention. His claims are as follows: (1) Grinding pyroxyline into a pulp, as and for the purpose described. (2) The use of finely comminuted camphor-gum mixed with pyroxyline pulp, and rendered a solvent thereof by the application of heat, substantially as described. (3) In conjunction with such use of camphor-gum, the employment of pressure, and continuing the same until the mold and contents are cooled, substantially as described.

Considering the claim that Daniel Spill was the inventor of celluloid, it is very significant that as late as the 11th of May, 1875, he took out a British patent 1739 of that year, for producing and applying Xyloidine. In this patent he makes no

references to any material that could possibly be called celluloid. On the contrary, he recommends the following mixture as a suitable solvent for soluble gun cotton or Xyloidine:

250 parts by weight of alcohol,  
150 parts by weight of ether,  
10 parts by weight of nitrobenzene,  
15 parts by weight of camphor or camphor oil  
250 parts by weight hydrocarbons, from coal, shale or other bituminous substances boiling between 220 and 400° F.

Or he says the following solvent may be employed:

400 parts alcohol,  
200 parts of hydrocarbons, before referred to, and 33 parts of camphor or of camphor oil.

Now this patent was taken out nearly five years after Hyatt's celluloid patent and although Spill in this patent suggests adding a small quantity of camphor to large quantities of other solvents, volatile and nonvolatile, he always mentions it as camphor or camphor oil, regarding them as equivalents. They certainly are equivalents for Spill's purposes to produce liquid solutions of pyroxyline, but camphor oil is not equivalent to camphor in Hyatt's process for making celluloid and it would be absolutely impossible to make celluloid by any process suggested in any one of these patents of Spill or Parks, or any other inventor prior to Hyatt, and this is what the federal judges decided when the matter was tried out in court.

Mr. Hyatt's activities were not limited to celluloid. Among his other inventions also of great importance, we find a sugar cane mill, very superior to any mill previously used, in its efficiency both in increasing the percentage of juice extracted from the cane and in greatly diminishing the time necessary to extract it, and in giving a higher value to the refuse bagasse as fuel.

In the early 80's, Mr. Hyatt and his brother Isaiah took up the subject of water filtration and started a company called the Hyatt Pure Water Company. Isaiah Hyatt invented and patented a very important feature of the filtration process, February 19, 1884, Patent 293,740. It marks the beginning of a new era in water purification. Coagulants had been previously used to purify water, but the difficulty was that the water was held in large tanks or cisterns. The coagulant was added to it, the whole was thoroughly agitated and then it was necessary to allow it to stand 12 to 24 hours for the coagulum to settle to the bottom. The Hyatts conceived the idea of employing a coagulant which could be added to the water while on its way to the filter, so that no large settling tanks or basins are required and no time is lost. The claim of this patent is as follows:

"The method herein described of arresting and removing the impurities from water during an uninterrupted passage of the same from a supply pipe into a filtering apparatus, thence through a filter bed contained therein and out through a delivery pipe leading therefrom, which method consists in introducing into the water simultaneously with its passage to or into the filter a substance which will sufficiently coagulate or separate the impurities to facilitate their arrest and removal by the filter bed, thus obviating the necessity of employing settling basins.

I was connected with a litigation which followed the issue of this patent, and studied the process and apparatus at Somerville, N. J., Niagara Falls and Elmira. The process was unusually successful. At Somerville the river water exhibited a milky opalescence caused by such fine particles of clay that no filter would clarify it. By a proper attachment of an alum box to the feed pipe to the filter, a minute quantity of alum was added to the stream of water on its way to the filter, less than one grain to the gallon, and in the few seconds that elapsed before the water reached the filter bed of the ingeniously constructed Hyatt filter, coagulation had taken place and the coagulum including the alumina of the alum and the clay, bacteria and other suspended impurities of the water had been converted into such flocks as made it possible for the bed of sand in the filter

to arrest it completely. These Hyatt filters are so constructed, whether they are on a large scale or small scale, that they can be washed completely at any convenient moment by simply reversing the current through the filter. This churns up the sand and separates from it the accumulated coagulum.

Nearly all the paper mills and woolen mills in the country were and still are supplied with these filters, as are also more than 100 cities and towns.

The validity of this patent was established through lawsuits which were brought against the cities of Elmira and Niagara Falls. These cities attempted to evade the Hyatt patents by constructing a chamber underneath the filter through which the water passed on its way to the filter, but we found by examination that while a portion of the coagulum accumulated in the chamber, one-third of it passed on and was separated by the filter. Judgments in favor of the Hyatt patent were given by the Circuit Court of the United States, Judge Shipman presiding, in 1894; by Circuit of Appeals, Judge Wise presiding, in 1895; again by Judge Cox in 1896; and again by Judges Wallace, Lacombe and Shipman in 1897.

In 1891-2 Mr. Hyatt took up the subject of antifriction roller bearings with great success.

I have really occupied far more time than I should have done, but I felt it a duty to take advantage of this opportunity to present the facts with regard to Mr. Hyatt's priority of invention in connection with the celluloid and water purification, which I was in a position to do owing to my experience and knowledge gained in the litigations which arose in both cases.

I think that the facts to which I have called your attention, although very briefly expressed, will satisfy you of the great achievements of Mr. Hyatt and will fully justify your committee in placing Mr. Hyatt beside Sir William Henry Perkin and the six American chemists who have already received the Perkin medal.

TO MR. HYATT:

It gives me great pleasure, as the representative of the Society of Chemical Industry, and the affiliated chemical and electrochemical societies, to place in your hands, Mr. Hyatt, this beautiful token of the appreciation and affection of your fellow chemists.

#### ADDRESS OF ACCEPTANCE

By JOHN WESLEY HYATT

MR. CHAIRMAN, LADIES AND GENTLEMEN:

I have never looked forward to any such honors as you have bestowed upon me, and I do not know how fittingly to express my gratitude. You have overlooked my lack of early training in the sciences with which you are all familiar, and look only to results which have been obtained mainly by persistent, and many times mistaken, experiments. Some successful experiments I might never have made if I had been familiar with the danger theories of some learned men.

#### CELLULOSE

From my earliest experiments in nitrocellulose, incited by accidentally finding a dried bit of collodion the size and thickness of my thumb nail, and by my very earnest efforts to find a substitute for ivory billiard balls, it was apparent that a semi-liquid solution of nitrocellulose, three-fourths of the bulk of which was a volatile liquid and the final solid from which was less than one-fourth the mass of the original mixture, was far from being adapted to the manufacture of solid articles, and that I must initially produce a solid solution by mechanical means. The only useful solvent known to me at that time was a mixture of alcohol and sulfuric ether; with the old formula (about equal parts of ether and alcohol) I mixed in a closed mill a thick paste of soluble cotton, made by the old firm of Charles Cooper & Co. After mixing, the cover of the mill was removed and the mass evaporated down to a thick dough, which was then forced

accurately around the ball (made of another substance), and allowed to dry. This I found resulted in a rather brittle coating, owing, as I found, to the unequal evaporation, leaving only the alcohol, a poor solvent by itself, at the final shrinkage. This was remedied by using only the least amount of alcohol (five parts ether to one alcohol) necessary as a solvent. Even this coating shrunk to less than half of its original thickness and required to be dried immersed in water under several hundred pounds' pressure per square inch to insure its solidity and freedom from bubbles. It became necessary to strain the mass by forcing it through a very fine sieve to exclude the unnitrated fibers. All these difficulties stood in the way of success, except in high-priced articles like billiard balls. Other seriously objectionable features became apparent. In order to secure strength and beauty, only coloring pigments were added, and in the least quantity; consequently a lighted cigar applied would at once result in a serious flame, and occasionally the violent contact of the balls would produce a mild explosion like a percussion guncap. We had a letter from a billiard saloon proprietor in Colorado, mentioning this fact and saying he did not care so much about it, but that instantly every man in the room pulled a gun.

I next had a small beating engine made, to pulp the nitrocellulose. In one experiment I placed a small quantity of this dried pulp in a strong cylinder and forced quickly a minimum quantity of liquid solvent into it with high pressure. The result was a solid substance, as hard as sole-leather, which soon dried, leaving a fine, hard disc about three-fourths of an inch in diameter and one-half an inch thick. While no explosion ever resulted from this, there was real danger to be feared, and the matter was dropped.

My brother, I. S. Hyatt, joined with me at that time, and finding it stated in some patents to which I was referred, that a little camphor added to the liquid solvent was beneficial, we conceived the idea that it might be possible to mechanically mix so vents with the pulp and coloring matter while wet, then absorb the moisture by blotting papers under pressure, and finally submit the mass to heat and pressure.

To our surprise, we noticed a slightly solvent action of the precipitated and washed camphor upon the pulp, even before the heat and pressure, and without other solvent we succeeded in producing a transparent slab one-fourth of an inch thick, fine, and as hard as a piece of wood. My brother took some samples to the American Hard Rubber Company, with the view of interesting them. They employed the late Professor Charles A. Seeley, who had made collodion for the government during the Civil War, to investigate the matter. He came to our place in Albany, N. Y., and we conducted the whole process for his inspection, very successfully. He remarked that he had come prepared to detect some chicanery, but could see no deception, and expressed himself as satisfied. He kindly advised us that if, accidentally or otherwise, we were to apply a little too high temperature, the quantity we were dealing with would inevitably destroy us with the building and adjacent property. While we did not accept this as true, it was disturbing. The following day between 12 and 1, when all were out, I rigged up a four-inch plank used as a vice-bench, braced it between the floor and ceiling, between the hydraulic press and the hand pump, intending it to shield me from possible harm. I then prepared the mould, heating it to about 500° Fahrenheit, knowing it would certainly ignite the nitrocellulose and camphor, and thinking I would abide by the result. The gases hissed sharply out through the joints of the mould, filling the room with the pungent smoke. The mould, press, building and contents were there, including myself, very glad that I did not know as much as the Professor.

The next step was to make a small stuffing machine, consisting of a cylinder, four-inch bore, about a foot long, termi-

nating in a tube three-fourths of an inch bore, ten inches long, immersed in an open oil-jacket, with a gas burner and thermometer. A capnut with one and one-fourth inch screw forced a plunger upon the cakes of incipient celluloid, which were heated at the outlet end of the cylinder passing through the heated tube into moulds, and also through nozzles forming rods, tubes, etc.

We found it advisable to lower the melting point of the camphor by adding a small quantity of alcohol or other solvent of camphor. A much larger hydraulic stuffing machine was then made. Dental plate blanks were the principal part of our early business.

My brother interested some New York capitalists—principally composed of General Marshall Lefferts, Joseph Larocque and Tracey R. Edson—and we moved to Newark, N. J., in the winter of 1872-73. We had nearly all the appliances and machinery to design and build, which progressed with some halts and mistakes for two or three years, when a fire occurred in our four-story and basement building, utterly destroying all our stock and machinery, pushing out the whole front of the building (which was very weak), and severely injuring several of our men, who all finally recovered, although one—Mr. Charles S. Lockwood—was in great danger for a long time. We then started our present works, acquiring knowledge and experience; my brother started a separate factory for making brushes, mirrors and combs. Early in 1878, my brother went to Paris and started the French Celluloid Company.

Before we left Albany we began the use of tissue paper in place of carded cotton or bleached flax, which finally resulted in getting tissue paper of definite thickness and materials, and breaking it up into small, separate pieces by a machine I constructed, drying these separate pieces in a loose mass and nitrating them instead of the carded cotton.

In 1876, I was allowed to employ a chemist for determining our acids and to systematize our nitration, instead of merely using hydrometers and thermometers, and Mr. Frank Vanderpoel was selected by me. So far as I know, the analyses of mixed spent acids was not reduced to practical work. Professor Seeley proposed that we separate the nitric and sulfuric acids by distillation, and then bring these to the proper strength before mixing, which was not adopted. Vanderpoel first removed the gelatinous flock by adding finely powdered natural barium sulfate and allowing the barium and flock to subside, which was a great success. I had previously tried filtration, which was impractical. After much labor Vanderpoel perfected a quick and accurate method of determination of the spent acids, and then added the required fresh acids. An elaborate and extensive battery of tanks was constructed, the acids being moved through copper pipes, where required, by means of air pressure. The tanks for mixing the comminuted tissue paper with the prepared acids were arranged on a turntable supporting a dozen or more tanks, each holding hundreds of pounds. A rotating stirrer was arranged to stir in the requisite amount of paper in one tank, the turntable being revolved to the next tank, and so on. At a distance embracing about half a dozen tanks from the stirrer was located a centrifugal machine; which separated out most of the acids. The nitrated paper was then thrown into a washing device, and the partly washed paper then fell into large tanks of fresh water and was thoroughly washed. A very considerable number of tons of paper per day were and are treated in this way.

The next procedure was to grind this nitrated paper in a beating engine. The water was then mainly removed by a centrifugal machine. The mixture of pigments, camphor and nitrocellulose was then made, according to the results required, and ground together in a mill, then pressed into slabs or cakes, still further deprived of moisture by great pressure, and finally deprived entirely of moisture by blotting papers, repeatedly



changed. These cakes were then broken up and alcohol or other desired solvents added and allowed to soak in. The partly dissolved mass was then masticated in heated rolls, turned out into necessarily rough sheets, cut into strips and rolled up into cylinders, ready for the stuffing machine.

The great need was for Celluloid in solid perfect sheets, and this neither the rolls nor the stuffing machines could possibly do, with all our experience. I constructed a special nozzle for the stuffing machine, to form a slab about one and one-half inches thick, seven inches wide and several feet long, which was pressed between steam plates, one of them with under-cut grooves to hold the slab. A machine was made with shaving knife and reciprocating bed, and by it the slab was shaved into sheets of the desired thickness. These slabs were necessarily imperfect, and were too small. After showing this result to the other directors, I proposed building a hydraulic pressure steam-heated mould, to make a slab or block about two feet by five, and three inches thick, in which to weld and press a pile of rough sheets from the masticating rolls.

General Lefferts, our much beloved president, had suddenly died a year or more before. To those who knew the least about Celluloid my suggestion looked pretty good, but to others came a great fear of possible danger and failure to weld up such a mass. At last they gave me authority to build the apparatus, limiting me to less than half its cost if fairly estimated. With this authority, which consisted more of the privilege of trying such an apparatus than in providing for its cost, I ordered the machine, agreeing to pay the machinist all above the appropriation if it failed to work. The machine was built and most carefully tried in the presence of only the new president, who knew little about celluloid, and Mr. Stevens and Mr. Lockwood from among the employees. The mould was cooled and opened, and nice sheets were at once made, considering that only scrap material was used, though less than half the block was welded. This meant reheating, which was at once done, and the whole was known to be a success.

I dwell upon this because of its vast importance to us. It multiplied the value of celluloid many times, making a much stronger and finer material than was produced by the former means.

About this time we were enjoined from bleaching the iron out of the pulp, caused by the iron-beating knives, and it was up to me to remedy the serious difficulty. A large revolving drum of copper, through the axis of which was a shaft with beating arms rotating at a very high speed, in which the mixture of nitrated paper, camphor and pigments was placed, and the whole beaten to a pulp without the discoloration of the iron and water, and without the loss in washing and bleaching the fine pulp from the beating engine.

In order to clearly differentiate my work in celluloid from that of others in the nitrocellulose industry, I will summarize as briefly as I can.

*First:* The idea of combining with the nitrocellulose only the exact or approximate amount of solvent required for a solid solution. This required a nearly perfect mechanical mixture before very much solvent action could take place.

*Second:* Completing the solution by means of heat and pressure.

*Third:* Eliminating the practically unnitrated fibers by pulping.

*Fourth:* Employing tissue paper in place of carded fiber.

*Fifth:* Avoiding the terrible danger of drying out the moisture by exposure in a drying room.

Many years ago I patented the process of first pressing out all the water possible and displacing the remainder by forcing alcohol through under pressure. This, I understand, is now used by other nitrocellulose workers, but we prefer the method herein described.

*Sixth:* The stuffing machine process.

*Seventh:* The sheeting process, most essential.

#### ACKNOWLEDGMENTS

Mr. Stevens has been with me ever since he was fourteen years old, has invented solvents and many other things of great importance in the art, and stands at the head of nitrocellulose workers at the present time.

Mr. Harrison, in his department, has invented the method of imitating the grain of ivory, of smoked pearl, of onyx, as well as many other beautiful colors and effects. He has been with us nearly forty years.

Others are entitled to much credit, but it is impossible to name them here.

#### SUGAR-CANE MILL

In the old method of milling sugar cane the cane is passed between rolls which are generally 34 inches in diameter and 84 inches long. These rolls are grooved and roughened so as to draw all the cane in between them that is possible. Owing to the comparatively obtuse angle formed by the contact of two rolls, the quantity of cane is limited and they are very nearly together at the passage of the cane through the last pair of rolls. The last, say 15 per cent, of the juice is forced out through five or six inches of highly compressed fiber in the opposite direction from which the cane is moving, so that in practice a considerable portion of the juice is carried through the rolls. For this reason it is repeatedly passed through rolls, at each passage removing a small proportion more of the juice. It is found profitable in most cases to add water to the bagasse between each set of rolls so as to dilute the juice that necessarily remains in the bagasse. In order to get the desired quantity of work from the mill, the rolls are of great length, from seven to seven and one-half feet. There are generally from 30 to 40 tons of pressure for each foot of face of the rolls. It is not practicable to get any greater pressure than this. I employ four or five times as much pressure per lineal foot.

With my apparatus and method the angle formed between the chain and the upper roll is far more acute and the cane is forced through rolls so that five times more cane goes through the rolls of a given face than is possible with the old mills. If this chain belt were impervious to the juice little or nothing would be gained by this method, but inasmuch as the chain forms a massive screen through which the juice may readily escape from the underside, the juice has only to pass downward through the mass perhaps one and one-quarter inches at the most to escape, instead of five or six inches in the opposite direction to the progress of the cane, as in the old mill. It does not take any more powerful apparatus to press the cane fiber when it is one inch thick than it does to press fiber that is one-eighth of that thickness, and as I get quite as much cane through my rolls with 12-inch face as will pass through the old rolls of 84-inch face I can readily afford to put several times as much pressure upon each foot of face as is practicable with the old mills. I employ upward of 150 tons on rolls with 12-inch face.

For the same amount of cane passing six times through the present rolls my mill will not require more than one-third as much power and instead of getting with the best milling a bagasse with 50 per cent of moisture and 50 per cent of fiber, I can easily produce a bagasse which has 60 per cent of fiber and 40 per cent of moisture. This bagasse is so dry that a quantity of it, either a handful or a bushel, placed upon the ground can be lighted with a match and will burn like carpenter's shavings. My mill is about one-eighth the weight of the present mills with the same capacity, and as the machine work is of the same character the machine will not cost one-quarter as much as the present mills.

In Cuba, 71 per cent of extraction without dilution is as good as can be obtained. With my mill, without dilution, I can easily get 78 per cent extraction. With Louisiana cane, which has less fiber, I can easily get 84 per cent extraction without dilution. Of course, if the bagasse is passed through a second mill with 12 per cent dilution, I can get 88 per cent extraction.

The joints of my sprocket chain belt are self-cleaning and cannot clog; as shown in practice, each revolution of the chain rubs the screen surface together several times. All the links of the chain are alike, and are of drop-forged steel. The concave edges of these links absolutely fit the under roll. The smaller pressing roll is provided with annular grooves coinciding with the longitudinal joints of the chain so that even the last small percentage of juice has a perfectly free outlet.

There is no danger from irregular feeding, as the mass of bagasse between the rolls is about one and one-quarter inches thick, and no loose or open space can possibly exist. The springs yield or follow up, according to the feed. No crusher or shredder is necessary or desirable.

The speed of the surfaces of the rolls and chains is designed to be 30 feet per minute, although I did practically as good work on my previous machine at 40 feet per minute, and it will probably be proved that this machine can do equally as good work at 40 feet per minute, but to be safe, I have calculated it for 30 feet per minute. The ordinary cane mills are run at anywhere from 16 to 25 feet per minute, according to the choice of the owner or engineer.

The increased value of the bagasse as fuel, and the avoidance of any peculiar kind of bagasse burner with forced draft, etc., are quite important items. Furthermore, as was shown by my machine at Adeline, Louisiana, the purity of the juice is considerably improved, as the cane is not ground up as in the ordinary mills, but merely flattened by the great pressure.

I have taken out 238 patents (a few of them being joint inventions with others), and several new industries have resulted. The one of next importance to celluloid is the Hyatt Roller Bearing. I have received considerable liquid money, most of it having been of a volatile and inflammable nature. Age ought to bring wisdom.

## PERSONAL REMINISCENCES

By FRANK VANDERPOEL

MR. CHAIRMAN, LADIES AND GENTLEMEN:

It is a great pleasure, I can assure you, to be present this evening, at a time when, in company with the preceptor whom all the boys of Columbia love, we are to do honor to my friend of later years, when what was taught me by the former became the equipment for my work with the latter. Every young fellow who had the good fortune to study chemistry under Dr. Chandler will bear me witness that the days thus passed were very enjoyable indeed: the memory of them will last long in our minds, no matter where, or in what circumstances we may find ourselves. When the request came to me from our worthy chairman to say something this evening at the presentation of this medal, I could not help feeling that there were other members of the societies which we represent who could do the subject more justice than I. There is no other, however, who is more gratified at the awarding of the medal. The only reason that I can think of for the selection of the speaker is that for a long term of years he has been the intimate friend and associate of the recipient of the medal.

Let me say, further, that when I was asked to take part in the exercises, it seemed almost as if I had been requested to assist at the obsequies of an old friend who had departed this life; for, of course, no one could be expected to say anything at such a time as this except in praise; anything else, even if it were possible, which it is not, would seem very ungracious indeed, and so, the recipient of the medal must listen, perforce, like Tom Sawyer and Huckleberry Finn, in Mark Twain's humorous story, when they came to their own funeral, to words of eulogy and praise of which he has never dreamed. However, let us dismiss

from our minds the thought that our friend is a departed one. He is very much alive: we haven't come here to bury him, and what we are about to say we are going to tell him to his face, and not apologize for it either. If you will permit personalities, Mr. Chairman, without which I don't believe I could get through with my talk, I should like to say that it was about three years after leaving Columbia that I had the good fortune to meet our guest of the evening. It happened at a time when I was desirous of locating myself where I could do laboratory work on a somewhat larger and more efficient scale than I had been able to do before. Without going into details, let me say that I met Mr. Hyatt, had a chat with him, found that he had discovered the need of an analyst at the works of The Celluloid Manufacturing Company, as it was then called, applied for such a position, and secured it through his kindness and influence. From that time until the present, and this means a long series of years, we have been friends, and our friendship has stood the test of sun and rain, of bright and cloudy days, of the ups and downs which every manufacturing business must have, and I think that we are as strong friends as ever, at this moment. In fact, I don't believe that there is anyone present who is more pleased than I am that the Perkin Medal has been awarded to him—unless it be Mr. Hyatt himself.

To refer to the early days of the celluloid business in Newark, where the factory was located, I should like to say that there seemed to be a good deal of prejudice against it in that city. On account of an unfortunate fire which took place there shortly after the company began operations, the people of Newark did not, as a rule, take kindly to a material which was reported as being made of guncotton and camphor. Of course, such a statement would never lose in transmission, and the people would look askance at any article of commerce which contained, as an ingredient, this high explosive. I remember hearing a story told of a man who happened to touch, with a lighted match, one of a pair of cuffs made of celluloid when, to his amazement, there was a terrible explosion, and he barely escaped with his life. Well, this and other stories of a like nature produced a strong feeling against the manufacture of this new substance, to say nothing of its use by the public, and, of course, some one had to bear the brunt of it. Naturally, the inventors (The Hyatt Brothers) and those most intimately associated with them in the business, had to carry the burden; and it wasn't a very light one, either. But our friend had the enthusiasm of the inventor, an enthusiasm which he imparted to those who were associated with him, and without which success would have been long delayed, if not impossible. I suppose that, in the minds of some, even at the present day, the idea exists that the principal ingredient in the material referred to is true guncotton, the highly-nitrated compound of cellulose. This is because the public, as a rule, is not given to distinguishing between the compositions of different chemical compounds. If, in order to make true guncotton, you treat cotton fiber with a bath composed of a mixture of strong sulfuric and nitric acids, why, it stands to reason—so some of these people think—that cotton fiber treated with a bath of these same acids, no matter what their percentage composition may be, will be converted into the explosive compound. You know that this is not the case, but the general public does not, or did not, some thirty years ago. If you will pardon the digression, I should like to say that, shortly after I became associated with the Celluloid Company samples were made of these two varieties of nitrocellulose, using raw cotton fiber in each case, and their solubility tested in a strong solvent, and thus compared. Any nitrocellulose which would not dissolve in this solvent would be utterly worthless as a basis for the manufacture of our product.

Upon making the test, the fibers of the lower nitrated compound disappeared in the solution upon the instant that they touched the solvent. This was the variety of nitrocellulose

which was the principal ingredient in the manufacture of celluloid. How long do you suppose it took the other, the true gun-cotton or trinitrocellulose (or, as some call it, hexa-nitrocellulose) to dissolve? It was kept in the bottle of solvent for more than six years without showing the slightest evidence of a solvent action—each fiber showing up bravely—then it was thrown away. But the public did not know of this difference and thought that the product of our friend's brain was a menace to every one who came near it. Prejudice goes far, and it takes courage and pluck to fight it. If I said much more on this point, you good people would think that the company had paid me to boom its product, which is not the case.

Mr. Hyatt's share in the work of making celluloid did not consist in merely getting out the various patents and handing them over to the company. He was often at the works, superintending, advising, assisting in the manufacture and always on call if things needed his attention. We all felt confidence in his judgment, and found afterwards that this confidence was not misplaced.

The inventor's enthusiasm is a valuable asset or adjunct in bolstering up the faint-hearted employee who may sometimes think that he has an idea of his own which he would like to have exploited. I think that more than one of the men employed at the works received encouragement from our friend, Mr. Hyatt, in certain lines of work in which they were engaged and which they might have been inclined to give up if it had not been for his enthusiasm and optimism. It not infrequently happens, in this world, that the success which a naturally timid person achieves is due, in some degree, to the encouragement which he may receive from one who has more courage and backbone. As the boys would say, "He doesn't get cold feet," and this means the difference between success and failure. We sometimes need optimistic friends who will help us over the rough places, or the thin ice—put it whichever way you will. Mr. Hyatt was one of these, I can assure you, and to his cheering influence is due, in great measure, I think, the success of the Celluloid Company. This comforting way of looking at things does not mean, let me say, that everything that a fellow would think of and suggest, would be endorsed by him. I well remember a remark made by him one day when I had occasion to relate how a certain so-called or self-styled chemist had utterly failed in the solution of a problem which he was *absolutely* certain he could solve. In fact, he claimed to have solved it some time before, but when a second attempt was made, the result was not in the least satisfactory. (Mr. Hyatt will pardon tales told out of school.) "Yes," said Mr. Hyatt, "a man may say to you, 'if I put this brick which I have here on this side of the street with that one over across the way, I'll have two bricks,' but when he goes across the street he finds that what he saw on the other side was not a brick, after all!" Very likely, Mr. Hyatt does not remember this occurrence, but, I assure you, it is true, as is also another one which happened at the works and illustrates his practical way of looking at things.

You know it is just as important, sometimes, to know what to omit as to know what to do: what to leave out of your invention as well as what to put into it. A mutual acquaintance, an employee of one of the branches of the Celluloid Company, went to our friend one day and told him of an invention which he had almost worked out in his mind, and asked his opinion of its value. He was going to make billiard balls out of celluloid, these balls to have a hollow centre, and this small cavity was to be partly filled with mercury, which, when the ball was struck, would act as a sort of brake on the motion of the ball and cause it to slow down. Mr. Hyatt's reply was: "Well, if billiard balls came ready-made and partly filled with mercury as you suggest, and you could find some way of getting that mercury out, I think that it would be a fine thing."

There was one element in Mr. Hyatt's make-up concerning which I cannot speak too highly, for the reason that you don't find it everywhere: it is, I believe, the exception and not the rule. It was his willingness to give every one credit for his own idea and not attempt to appropriate it himself. Sometimes he went further than this: he would take the thought that you gave him, enlarge upon it or improve it, and then hand it back to you as your own. How many do that to-day? I think that if you counted them on your fingers, you would have some fingers left over when you had finished counting.

No, indeed, there are probably several of us here to-night who can tell of cases where the true inventor has been coldly shoved to one side, and all the glory and honor appropriated by some one else.

There is another quality or characteristic possessed by the successful inventor which is a most important asset. Something which happened not very long ago on a train running across the Arizona desert may, in a slight degree, illustrate the point.

The day was hot and dusty, and anybody who has ever traveled those alkali deserts with nothing much in the way of vegetation but sage brush in sight, can tell you what that means. It is decidedly uncomfortable, to say the least, and you look in vain for a cool spot where your eyes may rest—a clump of trees, or a little running water. One of the passengers kept looking out of the window every minute or two, pulling the shade to one side as he did so, and then letting it drop back again into place. Another passenger, noticing the interested look on his face, asked him what he saw.

"I see miles and miles of corn, acres of wheat and cotton, and the whole country covered with farms," he said. "When the supply of water back of the tops of those mountains is tapped and brought down here to this prairie, we shall have it blossoming as the rose."

"What is your name?" the passenger asked.

"Luther Burbank," was the reply.

Now, what shall we call this quality or element in the composition of the successful inventor and advanced thinker along these lines? Some might say, "Efficiency." Well, that is a good name for it. It means making two; three or twenty cornstalks grow where none, or at the most only one, grew before. It means causing the dry and dusty desert to become a veritable garden. It means taking a product of the laboratory which, before, had been only a chemical curiosity, and working upon it in such a fashion, and with such determination that it shall become a most useful article of commerce which shall find application in a multitude of ways, and bring comfort, yes, and happiness to many a home.

Time will not permit me to tell of our guest's other achievements; his process for the continuous filtration of water; the roller bearings invented by, and named for him, and many other inventions for which the world is indebted to him. They are matters of record, and we know that they represent the product of a mind that is not content to remain idle but is at all times at work in the interests of the general public.

He has the faculty, often lacking in many well-meaning persons, of putting the right thing into the right place. You remember the story of the school boy who was reading "What a good time I am havin'." "What! Repeat that!" said the teacher. "What a good time I am havin'." "Why," said the teacher, "you are leaving out the 'g'." "Gee! What a good time I am havin'." Now, Mr. Hyatt differs from the boy, inasmuch as he generally gets the "g" in the right place. And, Mr. Chairman, ladies and gentlemen, I think that by placing the well-earned Perkin Medal in the hands of Mr. John W. Hyatt, you have put it in the right and proper place.



## CURRENT INDUSTRIAL NEWS

### EVALUATION OF PULPWOOD

In an address delivered by Martin L. Griffin, Chief Chemist of the Oxford Paper Co., before the Maine Section of the American Chemical Society in Bangor, Oct. 17th, Mr. Griffin shows how unsatisfactory the prevailing units of measurement in the lumber trade have come to be, when applied to the valuation of wood for pulp and he says: Dimension measure units are only properly applicable to dimension products, as lumber. When wood is to be valued for its yield in pulp, it should be measured in terms of its useful products like other commodities: as coal in heat units; ores in terms of their metallic content; fertilizers in terms of potash, phosphoric acid and ammonia.

Up to the present time manufacturers of pulp, buying wood upon the cord dimension unit, not only suffer by the variation in yield of pulp in the same, and different species, as spruce and balsam, but also by the uncertainty as to the solid contents of the cord.

**VALUATION BY VOLUME**—A cord of wood is defined to be a stack 4 ft. high and wide and 8 ft. long containing 128 cu. ft. The solid contents of such a cord are affected by various conditions, such as:

1. **LENGTH OF STICKS**—Sticks are never entirely straight and smooth, and in piling them one above another there always remain cracks, which become larger, the longer the sticks are and *vice versa*. With four feet sticks as standard, changes in the stick length, from one foot to six feet, vary the difference in the solid volume of the same stack measure from 14 per cent to 35 per cent.

2. **DIAMETER OF STICKS**—The smaller the sticks, the greater the number, and number of cracks to the cord and consequently less wood. The difference in solid volume of two stacks, whose sticks are twice as large in one case as in the other, may amount to 13 per cent; and if the sticks of the one are four times as large as those of the other, this difference may amount to 25 per cent.

3. **SPLIT WOOD**—Large sticks are often split to facilitate handling and drying. After splitting they cannot be stacked as closely as before. This swelling amounts to 5-6 per cent. As a rule, the longer and thinner the sticks split, the greater is the swelling of the stack.

4. **FORM OF STICK**—The straighter and smoother the sticks, the smaller the air spaces between them and consequently the greater the solid contents.

5. **SPECIES**—Soft woods contain on the average about 3 per cent more solid wood to the cord than hard woods, due to straighter habits of growth and smoother bark.

6. **GREEN AND DRY WOODS**—With the drying of wood there is a consequent shrinkage in volume. Green hard wood will shrink by completely air-drying from 9-15 per cent and dry soft, 9-10 per cent.

7. **PILING AND FIXING THE STACK**—The higher the stack the less closely can it be piled. The heavier the stick and the weaker the piler, the less close is the piling.

It has been observed that there is more solid wood in a stack when only one end supporting stake is used than when two are used. There always remains some space between the stakes holding the stacks together and the wood, therefore, the fewer the stakes supporting ends or the longer the piles, the more solid wood. Just here arise many controversies over wood measurements where the method of scaling in cars is employed. An ordinary freight car will hold three crosswise stacks in each end and one short lengthwise stack between, making the equivalent of seven short stacked piles having fourteen ends, about a cord to a stack. There are also many minor

details which affect the amount of solid wood in the unit measure.

Since it is obvious that each stick of wood involved cannot be scaled and the sum total in solid feet obtained, a method of drawing representative sample cords may be employed and these measured. A sample may not only truly represent a grade of quality, but when drawn at a proportional rate, it may as truly represent a quantity. Thus if every fifth stick is drawn as wood is running on a conveyor or in a sluice until one cord is gathered, we know that four other equal portions, alike in all particulars, have passed. Such a sample can be measured by any standard of value, including quality and substance. If such a mode of sampling is applied according to the theory of averages, the sample will represent the quality, and there remains only the counting of the whole number of sticks to determine with precision the total quantity in terms of any unit by which the sample is valued.

If all pulp wood were equally dry, of the same specific gravity, and would yield the same amount of fiber per unit volume, this method would be adequate. Such is not the case.

**VALUATION BY WEIGHT**—Bulk commodities are now very generally bought and sold by weight. Wood can be so valued and in many instances this method is easily applicable and has its advantages. According to the plan of valuing wood by solid volume as outlined, if we take the weight of the sample volume we approach much nearer the measurement of the substance. Such a sample weighing would be accurate and applicable alike to wood driven in the rivers or freighted by rail.

Where wood is shipped by rail, its weight adds another important factor, namely—the freight, and this must be paid by the mill. Here the weight and moisture test reveal the substance and the water upon which freight must be paid. A cord of spruce wood will weigh from 3300 lbs. to 4400 lbs. according as it has 35 per cent to 50 per cent moisture, and this difference in moisture may add 50 cts. per cord to the cost of the wood at the mill.

The author concludes his address by suggesting that buyers and sellers of wood get together and study their joint interests and at least save a large sum of money now paid to the railroads for hauling wet and green wood.

### PROGRESS IN THE FIXATION OF NITROGEN IN SCANDINAVIA

*The London Times Engineering Supplement* for Oct. 15, 1913, refers to the successful commercial development of the process for oxidizing ammonia to nitric acid by means of the catalytic action of platinum (see Eng. Pats. 698 and 8300 of 1902, and Addition to Fr. Pat. 317,544 of 1902; J. S. C. I., 1902, 548; 1903, 93, 420). The carbide works at Odda, Norway, when operations were started, comprised 10 furnaces, each with a capacity of 7-8 tons of carbide per 24 hours. Ten more furnaces, of 16-18 tons capacity each, have recently been added. The temperature is maintained at 5720° F. (3160° C.), the electrodes of the older furnaces taking 1400 kilowatts and those of the newer ones, 3500 kilowatts. It is stated that the radiation of heat from the new furnaces is less than from a steam boiler. The hot gases from the furnaces are used in the limekilns instead of producer-gas. The annual output, 32,000 tons up till recently, is now 80,000 tons of carbide. Most of this carbide passes direct to the calcium cyanide works of an associated company, which, at the present time, has an annual output of 80,000 tons, the number of furnaces having been increased nearly sevenfold since the opening of the works four years ago. The nitrogen used is prepared by the Linde process, 100 tons of air being liquefied daily. The furnaces have a capacity of 1 ton

each: the nitrogen is supplied through valves in the side, and a current at 60-75 volts through an electrode in the center. After about 24 hours at 1650° F. (900° C.), the carbide is converted into cyanamide, the resulting product containing 20 per cent of nitrogen. In addition to these developments, a company formed to acquire the rights of the Ostwald process (except in Westphalia and Rhineland) is erecting new works for the manufacture of carbide and cyanamide (and nitric acid) at Aura, Norway, with an estimated output of 200,000 tons of calcium cyanamide, and has acquired waterfalls at other places in Norway and also in Iceland, capable of furnishing power for an annual output of nearly 2 millions ton of calcium cyanamide. Works are to be erected at Dagenham on the Thames, at Trafford Park, Manchester, in Scotland, and in Ireland for producing from calcium cyanamide 12,000, 12,000, 9000 and 3000 tons of nitric acid, respectively. In the event of the supply of calcium cyanamide being curtailed or stopped, it will be possible to use the ammoniacal liquors from coke ovens, blast furnaces, residual recovery plant, and gas works as sources of ammonia.

### STANDARD SPECIFICATIONS FOR THE PURITY OF RAW LINSEED OIL FROM NORTH AMERICAN SEED

The American Society for Testing Materials, affiliated with the International Association for Testing Materials, has just issued a compilation of the reports of the Committee on Preservative Coatings for Structural Materials, D-1, 1903-1913. The following specifications for the purity of Raw Linseed Oil from North American Seed were adopted August 25, 1913:

#### PROPERTIES AND TESTS

1. Raw linseed oil from North American seed shall conform to the following requirements:

	Maximum	Minimum
Specific gravity at 15.5°/15.5° C. ....	0.936	0.932
or		
Specific gravity at 25°/25° C. ....	0.931	0.927
Acid number.....	6.00	
Saponification number.....	195	189
Unsataponifiable matter, per cent.....	1.50	
Refractive index at 25° C.....	1.4805	1.4790
Iodine number (Hanus).....		178

#### METHODS OF TESTING

2. The recommended methods of testing are as follows:

GENERAL.—All tests are to be made on oil which has been filtered at a temperature of between 60° and 80° F. through paper in the laboratory immediately before weighing out. The sample should be thoroughly agitated before the removal of a portion for filtration or analysis.

SPECIFIC GRAVITY.—Use a pycnometer, accurately standardized and having a capacity of at least 25 cc., or any other equally accurate method, making a test at 15.5° C., water being 1 at 15.5° C., or a test at 25° C., water being 1 at 25° C.

ACID NUMBER.—Expressed in milligrams of KOH per gram of oil. Follow the method described in *Bulletin No. 197*, revised 1908, Department of Agriculture, Bureau of Chemistry, page 142.

SAPONIFICATION NUMBER.—Expressed as with acid number. Blanks should also be run to cover effect of alkali in glass. Follow method given in *Bulletin No. 107*, revised 1908, Department of Agriculture, Bureau of Chemistry, pages 137-138.

UNSATAPONIFIABLE MATTER.—Follow Boemer's method taken from his "Ubbelohde Handbuch der Ole u. Fette," pages 261-262. "To 100 g. of oil in a 1000 to 1500 cc. Erlenmeyer flask add 60 cc. of an aqueous solution of potassium hydroxide (200 g. KOH dissolved in water and made up to 300 cc.) and 140 cc. of 95 per cent alcohol. Connect with a reflux condenser and heat on the water bath, shaking at first until the liquid becomes clear. Then heat for one hour with occasional shaking. Transfer

while yet warm to a 2000 cc. separatory funnel to which some water has been added, wash out the Erlenmeyer with water, using in all 600 cc. Cool, add 800 cc. of ether and shake vigorously one minute. In a few minutes the ether solution separates perfectly clear. Draw off the soap and filter the ether (to remove last traces of soap) into a large Erlenmeyer and distill off the ether, adding if necessary, one or two pieces of pumice stone. Shake the soap solution three times with 400 cc. of ether, which add to the first ether extract. To the residue left after distilling the ether add 3 cc. of the above KOH solution and 7 cc. of the 95 per cent alcohol, and heat under reflux condenser for 10 minutes on the water bath. Transfer to a small separatory funnel, using 20 to 30 cc. of water, and after cooling shake out with two portions of 100 cc. of ether; wash the ether three times with 10 cc. of water. After drawing off the last of the water, filter the ethereal solution so as to remove the last drops of water, distill off the ether, dry residue in water oven and weigh."

REFRACTIVE INDEX.—Use a properly standardized Abbé refractometer at 25° C., or any other equally accurate instrument.

IODINE NUMBER (HANUS).—Follow the Hanus method as described in *Bulletin No. 107*, revised 1908, Department of Agriculture, Bureau of Chemistry, page 136.

### URANIUM, RADIUM AND VANADIUM REPORT

The U. S. Bureau of Mines has just issued *Bulletin No. 70*. "A Preliminary Report on Uranium, Radium and Vanadium," by Richard B. Moore and Karl L. Kithil, of the Denver Laboratory of the Bureau of Mines. The bulletin describes the carnotite deposits, and gives the commercial methods of the treatment of ores.

Charles L. Parsons, Chief Division of Mineral Technology, says in the preface of the bulletin: "It has been shown that, although the Austrian Government has conserved its own resources of uranium and radium by purchasing the Joachimsthal mines and by carefully supervising pitchblende production, the deposits of radium-bearing minerals in the United States are being rapidly depleted by wasteful exploitation, chiefly for the benefit of foreign markets.

"Seemingly the country has been quite unaware of the extent to which uranium ores have been sent abroad. Investigation has developed the fact that during the year 1912, carnotite ores carrying 28.8 tons of uranium oxide were produced and that practically the entire amount was exported. The major part of this ore carried between 2 and 3 per cent  $U_3O_8$ , as it appears that no ore carrying less than 2 per cent can at present prices bear the cost of transportation. This means that 8.8 grams of radium chloride, or 11.43 grams of radium bromide, may be obtained from the ore shipped from this country in 1912. Only one American company has been preparing radium salts of a high degree of radioactivity and its product has only recently been offered for sale. The American ores exported were purchased for their radium content. It can probably be definitely stated that in 1912, there was obtained from American ores nearly two and one-half times as much radium as from all other sources combined.

"France, Austria, England, and Germany have their radium institutes fostered by their Governments or by philanthropic foundations. Up to the present time, although the United States has been furnishing a large part of the material for these foreign investigations, comparatively little has been done in the hospitals and laboratories of this country."

### THE APPROXIMATE MELTING POINT OF SOME COMMERCIAL COPPER ALLOYS

As very little information on the melting points of commercial brasses and bronzes can be found in either scientific or technical literature, tests of a few typical alloys were made by H. W.

Gillett and A. B. Norton, of the U. S. Bureau of Mines. The results, summarized, in *Technical Paper No. 60*, are as follows:

ALLOY	Approximate composition				Melting point	
	Copper	Zinc	Tin	Lead	° C	° F
Cun metal	88	2	10		995	1825
Lead-cun metal	85 1/2	2	9 1/2	3	980	1795
Red brass	85	5	5	5	970	1780
Low-grade red brass	82	10	3	5	980	1795
Leaded bronze	80		10	10	945	1735
Bronze with zinc	85	5	10		980	1795
Half-yellow-half-red	75	20	2	3	920	1690
Cast yellow brass	67	31		2	895	1645
Naval brass	61 1/2	37	1 1/2		855	1570
Manganese bronze					870	1600

The melting point given is the "liquidus," or point where the alloy is completely molten. The temperatures are thought to be accurate within  $\pm 10^{\circ}$  C. or  $\pm 20^{\circ}$  F.

### BUREAU OF MINES BUDGET

The estimate of appropriations for the United States Bureau of Mines, for the fiscal year ending June 30, 1915, as approved by Secretary Lane and forwarded to Congress, is as follows:

For general expenses, \$70,000.

Investigating mine accidents, \$347,000.

Equipment of mine rescue cars and stations, \$30,000.

Equipment of testing plant at Pittsburgh, Pa., \$10,000.

Testing fuels, \$135,000.

Mineral mining investigations, \$120,000.

Investigations of petroleum and natural gas, \$30,000.

Inspection of mines in Alaska, \$7,000.

Books and publications, \$2,000.

Lands, leases, etc., for mine rescue cars, \$1,000.

The total is \$752,000, an increase of \$90,000 over the fiscal year ending June 30, 1914.

### PLATINUM DEPOSITS IN GERMANY

Consul Thomas H. Norton reports that in several localities of the Ural Mountains, notably in the neighborhood of Nizhni Tagilsk in the Perm Government and about Mount Blegdat, platinum is found in sufficient amounts to allow of systematic mining operations. Very small quantities of platinum have been found in Borneo, Sumatra, Brazil, Colombia, Australia, and California, but the contributions from all these regions to the world's demands form a small fraction of the Russian supply—5 per cent or less. The total production is now about 13,250 pounds annually.

Every effort has been made in Russia to locate new deposits of the metal, but without success. The annual quantity tends to decrease, and an exhaustion of the deposits at no very remote date seems almost a certainty. At the same time, the demand for platinum has far outstripped the supply, and has naturally caused an enormous increase in the price. In 1892 platinum cost \$89 per troy pound, about one-third as much as gold. Four years ago the price had risen to \$338 per troy pound, and at present (October, 1913) it is \$488 per troy pound.

Under these circumstances a large group of industries will welcome the discovery in Germany of extensive deposits of platinum, susceptible of easy exploitation. The location of these deposits is at Wenden, in Westphalia, in a section where iron, lead, copper and zinc mines are abundant. While prospecting by drill in the neighborhood of Wenden, metallurgical chemists unexpectedly discovered appreciable amounts of platinum in the layers of rock covering the ores of the common metals. Over 100 analyses of different borings were made and all showed the presence of the metal in sufficient amount to guarantee profitable extraction. The amount of platinum present in the rock varies from 0.9 to 1.9 troy ounces per cubic yard, which is very rich compared with the Russian deposits.

Thus far a territory of 500 acres has been examined and the borings from nine different drill holes give on analysis the results cited. This tract alone will assure profitable extraction for many years. The depth to which the platinumiferous rock reaches has not been announced.

Steps have already been taken to begin the regular metallurgical extraction of platinum at Wenden on a large scale. It is thought that careful prospecting will reveal the presence of other extensive fields in the Westphalian ore region, where geological formations similar to those at Wenden are wide-spread.

Surprise may be expressed that in a country where chemical investigation is so highly developed, the existence of easily accessible platinumiferous rock deposits should have remained so long unsuspected. The reason is as follows: In the usual analytical methods, gold and platinum, as well as most of the rarer metals allied to platinum, are separated from the ordinary metals—iron, copper, silver, etc.—by treatment with nitric acid, in which the latter are soluble. Metallic gold and platinum remain behind as an insoluble residue after such treatment. They can be brought into solution by the aid of aqua regia, and be separated from one another, or the gold can be extracted by means of mercury. It happens, however, that platinum when alloyed with silver can be dissolved by treatment with strong nitric acid. As thus far platinum has been found in nature almost exclusively in the elementary form, no attempt has been made in ordinary ore analyses to test for the presence of the rare metal in the nitric acid solutions obtained as just described.

It seems, however, that in the Westphalian deposits platinum is present in the form of an alloy, and in the customary course of analysis entered into solution in the form of a nitrate. A chemist decided to test the solution of nitrates obtained in the normal course of an analysis for the possible presence of platinum, and this led to the unexpected discovery. There is every possibility that not only in Germany, but in all other countries, rock analyses will promptly be submitted to revision, and the greatest care taken to ascertain whether platinum is present. Deposits containing much less platinum than occurs at Wenden can still be worked most advantageously.

### U. S. MINERAL PRODUCTION, 1912

The value of all minerals produced in the United States in 1912, according to figures just compiled by Edward W. Parker, statistician, of the United States Geological Survey, reached the record-breaking total of \$2,243,630,326. This is more than six times the value of the production in 1882, 30 years ago. During that period the population has not quite doubled, but the per capita output of the mines has increased from \$7.27 to \$23.47.

### OIL-HARDENING PLANT IN NORWAY

Commercial Agent Erwin W. Thompson states that during the summer of 1913 an oil-hardening plant was opened at Fredrikstad by De Nordiske Fabriker, with head offices at Christiania. The original object was to harden whale oil for the soap industry, but as the result of experiments with edible oils the plant is being enlarged to a capacity of 1,000 barrels a day with the expectation of hardening cottonseed and peanut oils for the margarin makers. The Norwegian firm will purchase the best grades of cottonseed and peanut oils, and will also harden on toll.

### CONCENTRATED NITRIC ACID IN NORWAY

Consul General Charles A. Holder reports that 98 per cent nitric acid is being produced at the Notodden and Rjukan plants where they now manufacture calcium nitrate. The acid has already been used successfully by factories manufacturing explosives. The manufacture of this concentrated acid is expected to prove of great importance.



### PROPOSED BEET-SUGAR FACTORY FOR CHILE

Consul Alfred A. Winslow, Valparaiso, reports that the cultivation of sugar beets is receiving much attention of late in Chile, and a movement is on foot to interest capital for the erection of a beet-sugar factory. Sugar beets have been successfully raised at several points in this Republic, yielding 15 per cent and more of sugar.

As early as 1880 beet sugar was manufactured in a small way at Nunoa, Chile, and again from 1885 to 1891 at Los Guindos, and as late as 1901-1904 at Membrillo. While production on such a small scale was not found profitable, it was demonstrated that a factory of a capacity of 700 or 800 tons of beets per day could be made to pay well at the present rate of protection of 68.5 cents or 59.9 cents United States gold per 100 pounds on raw sugar, according to quality.

The following table shows Chile's imports of the different classes of sugar:

Pounds of sugar	Refined	White	Granulated	Crude
1906.....	17,714,521	1,449,363	95,567,956	1,994,740
1907.....	10,989,207	2,174,744	108,258,612	1,942,589
1908.....	6,873,592	2,659,778	94,607,942	1,134,760
1909.....	10,265,046	2,353,340	136,874,188	2,313,410
1910.....	9,233,046	1,678,732	143,935,352	1,684,595
1911.....	4,797,045	4,050,464	154,984,306	2,589,510
1912.....	6,009,861	3,262,116	136,327,268	1,749,440

Practically all of the crude sugar comes from Peru and is refined in Chile, since the duty on refined sugar is \$1.64 or \$1.09 United States gold per 100 pounds, according to quality.

### PRODUCTION OF PORTLAND CEMENT IN 1913

It is estimated by Ernest F. Burchard, of the United States Geological Survey, that the quantity of Portland cement manufactured in the United States in 1913 was approximately 92,406,000 barrels, compared with 82,438,096 barrels in 1912, an in-

crease of about 9,967,900 barrels or 12 per cent. The estimated shipments of Portland cement during 1913 were 88,853,000 barrels, compared with 85,012,556 barrels in 1912, an increase of about 3,840,400 barrels, or 4.5 per cent. On account of a large surplus of production over shipments, stocks of cement at the mills apparently increased more than 45 per cent, or from 7,811,329 barrels in 1912 to 11,375,000 barrels at the close of 1913. In 1913 the relations between production and shipments were the reverse of those for 1912, when shipments exceeded production. It may be necessary to revise considerably the estimates of stocks, but it is believed that these figures for production and shipments are very close to those that will be shown by complete returns from all producers.

Although few definite statements as to selling prices are at hand it is evident that the average value per barrel was appreciably higher than in 1912. Increases of 10 to 25 cents a barrel are reported from several plants in the central and eastern states, but there were slight decreases reported from a few plants in the Rocky Mountain district.

### NATURAL GASEOUS MIXTURES RICH IN HELIUM

According to the *Journal of the Franklin Institute*, the following natural springs evolve gas containing a large percentage of helium. The natural gas from the springs at Sautenay contains from 8.4 to 10.1 per cent of helium, that from springs at Mai-zières contains 5.9 per cent; from springs at Grisy, 2.18 per cent; from Bourbon Lancy, 1.84 per cent; from Nérís, 0.97 per cent; and from La Bourboule, only 0.1 per cent. The quantities are too large to be considered as nascent helium evolved immediately it is produced; and it is more probable that the immediate source is dissolved helium, evolved by the disintegration of minerals in which it has been absorbed. These sources are grouped in the neighborhood of Moulins, Dijon, and Vesoul, France.

## NOTES AND CORRESPONDENCE

### PURIFICATION OF WATER BY ADSORPTION. PRELIMINARY ANNOUNCEMENT

Lead may be removed from water by shaking the water with fuller's earth, or similar adsorbent, and then filtering through paper. A sample of water drawn from a lead pipe which contained 1.5 mg. lead per liter, and which was entirely free from turbidity, so that the lead was probably present in true solution, required 0.05 mg. earth per 100 cc. and exposure to the earth for three minutes exclusive of the exposure incidental to filtering for complete removal of the lead. Lead was also removed from dilute solutions of lead acetate by means of fuller's earth, powdered charcoal, powdered pumice stone, powdered talc, ferric oxide, and marine clay, but quantitative determinations have not yet been made. Of these substances fuller's earth appears to remove lead best.

Bacteria are also removed from water by agitating it with adsorbents and then filtering through paper. Water containing 24,000 bacteria per cc. was rendered entirely sterile by treating 100 cc. for 15 minutes with 1 gram powdered charcoal. The same amount of fuller's earth per 100 cc. water reduced the total count very much but did not remove all bacteria. Larger amounts of earth effected complete sterilization. The complete removal of bacteria by means of any of the substances, fuller's earth, charcoal, or pumice, depends upon the two factors, amount of adsorbent, and length of time the water is treated before filtering. Fuller's earth appears to serve best for removing lead, and charcoal for bacter a.

Fuller's earth imparts a decided taste to water which cannot be removed by several previous extractions of the earth with water either hot or cold. It may be removed, however, by heat-

ing the dry earth, or by extracting the earth with concentrated hydrochloric acid containing a little nitric acid, and then with boiling water. The taste from charcoal is much less marked than that from raw fuller's earth, but charcoal is much more dirty to handle. Water treated with the sample of pumice used acquired only a slight taste, which can be removed by heating the pumice first. Clay and ferric oxide both gave a strong taste. In deciding whether a particular adsorbent gives a taste, it should be remembered that many varieties of filter paper, unless previously extracted for some time, will impart a slight taste to a solution passed through them. It is believed that treating with some adsorbent and filtering through paper, can be used to purify small amounts of water for drinking purposes, and may be adapted especially to the needs of travelers, and to household use during epidemics.

We are indebted to Dr. F. N. Whittier for assistance in making some of the bacteriological tests. The work will be continued.

BOWDOIN COLLEGE  
BRUNSWICK, MAINE  
JANUARY 7, 1914

MARSHALL P. CRAM  
HENRY D. EVANS

### NOTE ON CERTAIN UNPUBLISHED WORK ON ELECTROLYSIS USING SUPPORTED MERCURY KATHODE<sup>1</sup>

I commenced work towards a commercial solution of the wet electrolysis of common salt in 1888 and my first efforts were devoted to the mercury kathode, the results obtained in that year being what I propose to describe. At that time all the

<sup>1</sup> Presented at the 6th Annual Meeting of the American Institute of Chemical Engineers, The Chemists' Club, New York, December 10-13, 1913.

rugged appurtenances of a successful commercial apparatus were yet to be developed in order to lift any process for the purpose out of the laboratory. It, therefore, came about that, in considering the immense distance to be traveled in order to surround the invention of the supported mercury cathode with the necessary concomitant equipment, and in the light of certain simplifications possible when using the diaphragm process, I gradually worked over to devoting myself exclusively to the development of the latter. It may not be out of place to say that it was this development which became, less than five years later, the first commercial contributor of caustic soda and chlorine to the world's markets<sup>1</sup> and which, if I may be allowed to say so, embodied those essential features of diaphragm success (such as excess liquid pressure on the anode side) which have since been used by everyone working in this field.

Referring to the 1888 work, it seemed to me obvious that, with a view to eliminating sodium from the solution, the worst possible place to put it was on top of a layer of mercury exposed to contact with said solution. The point is that, although sodium dissolves in mercury, the initially formed amalgam is of very low specific gravity compared with mercury itself and naturally tends to stay on top of the latter save as a sluggish tendency to diffusion operates otherwise. It seemed to me that the obvious alternative was to use the under side of the mercury as the cathode, the upper side being completely exterior to the electrolyzer as such, with the idea that the sodium, as fast as it was delivered to said under side, would bob up to the upper side and be thereby removed from relation with the electrolyzer and its contents.

This I proceeded to do, using a horizontal square frame of paraffined pine wood, a supporting sheet of a special cotton fabric carried by the under side of said frame, and additional support supplied to the fabric by a paraffined wood grating. Mercury was placed on the fabric to a depth just sufficient completely to cover it and a current supplied from a primary battery of three large two-fluid bichromate cells between a carbon anode and the under side of the mercury, saturated salt brine being the electrolyte.

The first run made with this cell will always be a painful memory. I started it on a certain Sunday morning in July and then went off for a walk to a point 7 miles distant. Returning in the evening I looked at the cell and saw to my disgust that the mercury was covered with liquid and that there were grains of some white material resting on the mercury in said liquid. I jumped to the conclusion that the layer of mercury had become discontinuous and that hydrostatic pressure had forced brine up over it and that partial evaporation had precipitated crystals of salt. Just to see what it tasted like I put my finger in the liquid and touched it with my tongue and then removed it with speed because the liquid was an oily 50 to 60 per cent solution of C. P. caustic soda and the white grains were undissolved particles of same. Of course what had happened was that sodium had entered the mercury from the under side and oxidized and hydrated, in moist air, from the upper side, and a portion had deliquesced in additional moisture abstracted from the air. I have always felt convinced that this general principle would work up to the best possible type of mercury cathode electrolyzer, but I also took the view, at least in the 90's, that unless some great commercial advantage accrued from being able to supply C. P. caustic, the best diaphragm process could, on the whole, do better than any process using a mercury cathode. However, seeing that mercury cells are in considerable use I am unable to understand why the apparently obvious principle above described has not been employed. In the light of the principle so clearly grasped in connection with the above quarter century old work, it is curious to note, in Wilderman's address before the World's Congress last fall, the repeated re-

marks on the disadvantages all processes previous to his have labored under of putting the light sodium in on the top layer of mercury and leaving it there.

### SYNTHETIC RESINS

*Editor of the Journal of Industrial and Engineering Chemistry:*

IN THIS JOURNAL, 6, 3 appeared a paper by L. V. Redman, A. J. Weith, and F. P. Brock, which is supposed to be a general review of the literature on phenolic-methylene-condensation products, together with the results of personal research work of the authors.

The paper in question would have had increased importance if some of the opinions and statements expressed therein were more in accordance with facts.

The paper, although dated from the University of Kansas, is no more nor less than one of the so-called industrial research fellowships inaugurated by Professor Duncan, and which are paid for in the interest of purely commercial enterprises. In the paper, the author refers to "our firm, S. Karpen & Brothers, of Chicago," which tends to offset somewhat any prestige the mention of the name of the University of Kansas may bring about.

Among the several erroneous statements which are to be found in the paper, I shall mention more particularly the following:

On page 6, second column, paragraph 11, referring to the use of hexamethylenetetramine, it is stated that the British patent Wetter (Lebach) "shows clearly that this reaction is no other than a water process to which a condensing agent has been added." In reality, the patent in question says nothing of this kind; the text clearly (on page 3, lines 50, etc.) reads as follows: "The 40 per cent formaldehyde may be replaced also by its polymerization products, as well as by substances which yield formaldehyde, such, for example, as hexamethylenetetramine."

On page 7, first column, the paragraph entitled "Problem," recites a problem where the authors show a fertile imagination, untrammelled by mere cold sober facts. For instance, they state: "The resins formed (by the dry process as claimed by the authors) have very great commercial possibilities on account of their uniformity, chemical inertness, dielectric properties, mechanical strength, high refractive index (luster), plasticity at certain stages and the cheapness and supply of the raw materials from which these resins are manufactured."

In how far this statement is in accordance with the real facts, is shown further by direct comparative measurements and tests; it will be demonstrated that it matters not whether the process is carried out wet with my older process, or dry according to the directions of the authors.

The last sentence, referring to "the cheapness and supply of the raw materials," looks rather awkward in so far as it refers to hexamethylenetetramine, which is manufactured from formaldehyde and ammonia, followed by evaporation, crystallization and drying. How this is a cheaper raw material, or a better supplied material than a plain mixture of ammonia and formaldehyde, is beyond my understanding.

Further down (page 7) a rather narrow and arbitrary construction is put on the definition of the word "bakelite." The fact is overlooked that "bakelite" is merely a registered trademark name for phenolic condensation products. It is true that in my first publication on this subject<sup>1</sup> I have referred, as a typical example of bakelite, to a product resulting from the union of 6 molecules of phenol and 7 methylen groups, which shows good resistance to acetone, while similar products containing more phenol seem to contain, at the same time, salitren products which weaken their resistivity to acetone. For tech-

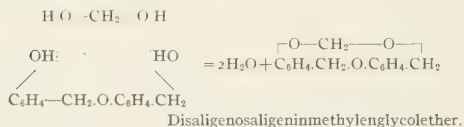
<sup>1</sup> Parsons, *J. Am. Chem. Soc.*, 20 (1898), 868.

<sup>1</sup> THIS JOURNAL, 1, No. 3, 1909, page 147.

nical purposes, however, many kinds of bakelite are manufactured, some of them containing more phenol, others containing homologs of phenol, others again containing a considerably larger amount of methylen-groups.

In my Willard Gibbs lecture<sup>1</sup> I pointed out this fact as follows: "This simple way of interpretation has the advantage that it accounts for the possible existence of any number of similar bodies made with a varying proportion of formaldehyde. For instance, it leaves the possibility of imagining that a product may exist which is derived from more than six molecules of oxybenzylalcohol and one molecule of methyleneglycol, which then would show less chemical resistivity. In the same way, it allows conception of varieties of the same product with a smaller number of molecules of phenol-alcohol entering into reaction with one molecule of formaldehyde or methyleneglycol.

"Numerous facts point to the existence of such modified bodies of which the chemical and physical inertness increases with the lesser amount of molecules of phenol-alcohol, which enter into reaction with one molecule of methyleneglycol; or to put it simpler, of which the resistivity increases with the larger amount of formaldehyde which reacts with a given amount of phenol. Dr. H. Lebach [*Z. angew. Chem.*, **22**, 1599 (1909)] called attention to the existence of a condensation product resulting from the action of one molecule of methyleneglycol (formaldehyde) on disaligenosalginen:



"The latter corresponds, in practice, to condensation products resulting from the direct reaction of two molecules of phenol on three molecules of formaldehyde."

Some of these varieties of bakelite, containing more methylen groups, have been manufactured here and abroad for certain purposes, and are characterized by a considerably increased resistivity, especially towards caustic alkalis.

The statement that dry hexamethylenetetramin and dry phenol heated together evolve no water, may have a theoretical significance, but it does not alter the fact that large amounts of gaseous ammonia are set free, and that the ammonia is even more troublesome than water, as far as the technical applications are concerned. But right here my patented process for the conjoint use of heat and pressure becomes of paramount value, because its practice obtains homogeneous articles, where otherwise a porous useless mass would be the result.

With the use of much smaller amounts of ammonia, or other alkalis, homogeneous products can be obtained at relatively low temperatures, without the use of pressure, and this is one of the advantages of the use of small amounts of bases.

On page 8, paragraph 3, the authors avoid the disturbing influence of ammonia, by producing a porous mass of material B, or "intermediate product," and then welding together the ground-up material in a hot hydraulic press. They omit, however, to refer to my two United States patents Nos. 939,966 and 942,700, where this process is very accurately described.

On page 8, second paragraph, second column, the statement occurs: "This reaction between a phenolic body and an active methylene group may be followed by simply measuring the amount of ammonia which has been evolved." Instead of stating: "This is especially true if the phenol is in excess," the correct thing would be to state that it is *only* true in case phenol is in *large* excess. Under the latter conditions, a permanently fusible, soluble resin is formed—a "novolak."<sup>2</sup> Then indeed,

the elimination of ammonia during the heating process is complete, and the amount of ammonia evolved becomes an accurate indication of the progress of the reaction. But such is not the case if less phenol be used, because then an infusible, insoluble product is formed, which is totally different in chemical composition and in general properties, and which retains a considerable amount of ammonia in the final product. The evolution of this ammonia gas keeps on to the moment when the product solidifies to an infusible porous mass. But here again, my patent for the conjoint use of heat and pressure, No. 942,700, comes in most handy whenever technical applications are concerned.

That part of the paper which describes the method of producing Novolak by the action of small amounts of hexa, on an excess of phenol, gives also the analysis of the resulting fusible resin. If we take into consideration the difficulty of this class of chemical investigation, the recorded results confirm, to a remarkable degree, the data and conclusions at which I arrived in my paper, "On Soluble, Fusible Resinous Condensation Products of Phenols and Formaldehyde."<sup>1</sup> The authors substitute the long name of "phenyl-endika-saligeno-saligenin," for the shorter name "novolak."

It seems to me that the authors might have done better justice to Dr. C. P. Steinmetz, of Schenectady, N. Y., by mentioning that this method for making a permanently fusible resinous condensation product, was described in all its details, by him, in his pending patent application of which Dr. Redman got knowledge during the interference proceedings before the United States Patent Office, in which Dr. Steinmetz, Mr. Byron Goldsmith, as well as Dr. Redman, and myself are contesting parties.

As to the transformation of this or any other Novolak into infusible products by further heating with methylen-containing bodies, like paraform, hexamethylenetetramin, etc. (see page 10, column 2, last paragraph) this is a well known and well described process, patented by Mr. Aylsworth, as well as by myself.<sup>3</sup>

On page 9, second column, occurs this statement: "We have, at present, in our laboratory rods of this material 2 feet long and 1 1/2 inches in diameter which have been produced by simply pouring the material while liquid into open molds and allowing it to harden under suitable heat treatment without the application of external pressure. These rods in the final condition are homogeneous, almost water white transparent and free from fractures or gas bubbles." This statement would be more significant if it were accompanied by some data as to tensile strength or brittleness of this product, or if it were stated at the same time, that its method of production was not borrowed from some other existing patents.

As to the table of analyses published on page 11, first column, some of the results relating to bakelite products are strikingly inconsistent with all the theoretical speculations of Dr. Redman; for instance, "a bakelite pipe stem bought in the open market" shows a higher percentage of material insoluble in KOH than any of the materials made with dry phenol and dry hexamethylenetetramin, although the latter product is vaunted to be an improvement over the first.

The apparatus described on page 11, for determining whether water is set free when reacting with an excess of phenol on hexamethylenetetramin, seems to invite a very serious objection as to the suitability of this method. Indeed, the inverted condenser designated by 8 seems to be the best means for *preventing* any formed water to enter into the train of absorbing tubes where the water is supposed to be determined. Furthermore, it is a well known fact that pure phenol has a decided tendency to retain small amounts of water and this even at high temperatures.

It should be noted that in these condensation products, it is not a matter whether 10 or 5 per cent or even 1 per cent of

<sup>1</sup> THIS JOURNAL, **1**, 545

<sup>2</sup> Aylsworth, U. S. Patent No. 1,020,593; Backland, U. S. Patent No. 1,038,475.

<sup>3</sup> THIS JOURNAL, **5**, 506

<sup>4</sup> *Ibid.*, **1** (1909), page 545.





have practically the same specific electrical resistance and the same surface conductivity.

If we add that all the infusible materials made from phenol (hydroxybenzol) and formaldehyde and ammonia, or hexamethylentetramin, dry or wet, have the same specific gravity, the same color, the same appearance, the same resistivity to solvents and chemicals, and that up till now, no property has been mentioned which is not common to all these products, it becomes easy to draw conclusions as to their absolute identity.

L. H. BAEKELAND

YONKERS, NEW YORK  
January 10, 1914

## OZONE

*Editor of the Journal of Industrial and Engineering Chemistry:*

Referring to the editorial, on the above subject (THIS JOURNAL, 5, 882), commenting on tests of ozone published recently in the *Journal of the American Medical Association*, I wish to call to your attention that the manner in which these tests were conducted, leaves large room for doubt as to the reliability of the conclusions drawn by the authors and that the readers of your valuable paper should be warned against accepting them without more convincing proof.

After a careful study of the reports, I am impressed that many of the conclusions are imaginary and not proven by the results obtained. For example, tests were made on three men by placing them individually in front of a large ozone generator delivering a strong blast of ozonized air at high concentration, the face of the victim being only a few inches from the outlet of the ozone generator. One of the victims had a "sore throat" ("cold") at the beginning of the experiments. The experimenters concluded from the results of the test that breathing ozone in strong concentrations produces sore throat. When we consider the probable effect of the blast of air on the face and head, the wind pressure on the nasal passages and the dust carried by the blast, it seems rather far-fetched to make any definite conclusions regarding the effect of ozone, especially from such a small number of tests and subjects. Furthermore, the conditions of the tests were extremely abnormal as it has not been proposed to use in ventilation concentrations exceeding one-tenth of that used in these tests.

The results of the bactericidal tests indicate that ozone in dry air has little germicidal effect. There is, however, overwhelming evidence which proves beyond a doubt that it will destroy germs in water. This has been thoroughly tested out by the best scientific authorities in Europe in connection with the many municipal ozone water purification plants, as well as by Pasteur's Institute and the German Imperial Board of Health. The latter were able to destroy by means of ozone practically all germs in water containing as many as 30,000 cholera and 30,000 typhus bacteria per cubic centimeter. As there is always considerable moisture in the respiratory passages, it is perfectly logical to suppose that the breathing of ozonized air may have some beneficial effect.

The fact that the guinea pigs died in an atmosphere of strongly concentrated ozone is not surprising, as there is no substance known to science which will destroy bacteria without also destroying animal tissue. For this reason, antiseptics cannot be used all strength and the best that is expected from their use is to stunt the growth and prevent the propagation of the bacteria.

The tests on the animals in the cages supplied with mild concentrations of ozone showed practically neutral results, i. e., there was no pronounced beneficial or detrimental effects noted. The duration of the tests was entirely too short to be conclusive.

The test these experimenters made of blowing ozonized air on a piece of paper covered with lampblack to determine the

effect of ozone on tobacco smoke, was going a long way around. It seems to me the proper way to make such a test would be to make it on tobacco smoke instead of lampblack. Particles of carbon in lampblack are very many times larger than the floating particles of tobacco smoke and hence, the oxidation of the latter in its very finely divided state might take place when lampblack would not be appreciably affected.

W. H. THOMPSON

WESTINGHOUSE ELECTRIC & MFG. CO.  
EAST PITTSBURGH, PA.  
December 16, 1913

## RAPID DETERMINATION OF COPPER IN STEEL, CAST IRON AND ALLOY STEELS

*Editor of the Journal of Industrial and Engineering Chemistry:*

The steadily increasing use of copper in steel in the last year or so has created a demand for a more rapid determination of that element in steel than is possible by the present method of analysis.

Copper in steel is usually determined by being precipitated as copper sulfide by the means of hydrogen sulfide or sodium hyposulfite. The copper sulfide is then generally incinerated in a porcelain crucible, digested at a gentle heat with nitric acid, transferred to a platinum crucible and evaporated with hydrofluoric and sulfuric acids to remove silica.

The residue, if not soluble in sulfuric acid, is fused at a low heat with sodium or potassium pyrosulfate. The copper is then deposited electrolytically from the acid solution, or determined colorimetrically in an ammoniacal solution.

In the presence of titanium and molybdenum there are variations of this method which make it even more tedious and time-consuming. There is nothing new or original claimed for the method about to be described as it follows very closely Low's method for the precipitation of copper by aluminum, but so far as the writer is aware, it has never been used for the determination of copper in steels or irons.

### METHOD

From three to five grams of steel, depending upon the amount of copper present, are dissolved in a mixture of 60 cc. of water and 7 cc. of sulfuric acid (sp. gr. 1.84) in a 250 cc. beaker. After all action has ceased, place in the beaker a piece of sheet aluminum prepared as follows: Cut a stout piece of sheet aluminum  $1\frac{1}{2}$  inch square and bend the corners so that it will stand upon its edge in the beaker.

Boil the solution from twenty to twenty-five minutes which will be sufficient to precipitate any amount of copper liable to be present. Remove from the heat and wash the cover and sides of the beaker with cold water. Decant the liquid through a S & S 11 cm. filter. Wash the precipitate three times with cold water, then place the filter in a 100 cc. beaker. Pour over the aluminum in the beaker 8 cc. of nitric acid (sp. gr. 1.42) and 15 cc. of water and heat to boiling. Pour this over the filter in the 100 cc. beaker and boil until the paper is a fine pulp, which requires only a few minutes. Remove from the hot plate and filter, wash with water, receiving the filtrate in an electrolytic beaker, add 2 cc. of sulfuric acid (sp. gr. 1.84) and electrolyze, using 2 amperes and 2 volts. Gauze cathodes and anodes are used and the deposition is completed in from one to one and a quarter hours. The total time of the determination from the weighing of the sample to the weighing of the copper is about three hours, and with the proper equipment, a large number of samples may be run at the same time.

Below are some of the results obtained on the Bureau of Standards' samples.

Name	Average copper present Per cent	Copper found Per cent
Vanadium steel No. 24.....	0.022	0.020
Chrome nickel steel No. 32.....	0.056	0.056
Chrome vanadium steel No. 30.....	0.070	0.066
Nickel steel No. 33.....	0.150	0.150
No. 5 A iron (C).....	0.060	0.063

As a further proof of the accuracy of this method, known amounts of pure electrolytic copper containing 99.88 per cent of copper were added to the Bureau of Standards' sample No. 14 A steel. The mixed drillings were dissolved in 20 cc. of (2-1) nitric acid, 8 cc. of sulfuric acid (sp. gr. 1.84) added and the solution evaporated until sulfuric acid fumes were evolved freely. The solution was allowed to cool and then 25 cc. of cold water were added and the solution was heated until all the sulfate was dissolved. The solution was filtered and the filter washed with hot water. The volume (not to exceed 75 cc.) was brought to a boil and the sheet aluminum introduced. Procedure was the same as stated before, except that after the solution was decanted through the filter and washed with water, the copper was dissolved on the filter and the filtrate received in an electrolytic beaker and electrolyzed as usual. The results obtained follow:

Copper added Per cent	Copper found Per cent
0.499	0.49
0.998	0.99
1.997	1.97
2.996	3.00
3.995	3.99
4.994	4.98

I wish to give credit to Mr. George Shuster of the laboratory force, who tried out this method and obtained the results stated above.

WILLIAM B. PRICE

WATERBURY, CONN.  
Oct. 25, 1913

#### INTERNATIONAL ELECTRICAL CONGRESS, 1915.

The International Electrical Congress is to be held at San Francisco, September 13-18, 1915, under the auspices of the American Institute of Electrical Engineers, by authority of the International Electrotechnical Commission and during the Panama-Pacific International Exposition. Dr. C. P. Steinmetz has accepted the Honorary Presidency of the Congress. The deliberations of the Congress will be divided among twelve sections which will deal exclusively with electricity and electrical practice. There will probably be about 250 papers. The first membership invitations will be issued in February or March, 1914.

Attention is drawn to the distinction between this Electrical Congress and the International Engineering Congress which will be held at San Francisco during the week immediately following the electrical congress. The engineering congress is supported by the Societies of Civil, Mechanical and Marine Engineers and by the Institutes of Mining and Electrical Engineers, as well as by prominent Pacific Coast engineers who are actively engaged in organizing it. This Congress will deal with engineering in a general sense, electrical engineering subjects being limited to one of the eleven sections which will include about twelve papers, treating more particularly applications of electricity in engineering work.

The meeting of the International Electrotechnical Commission will be held during the week preceding that of the Electrical Congress.

#### SPRING MEETING OF THE AMERICAN CHEMICAL SOCIETY

The Forty-ninth General Meeting of the American Chemical Society will be held in Cincinnati, Ohio, April 8-11, 1914.

The officers of the local section are: President, F. W. Weissmann, 2900 Vine St., Cincinnati, Ohio, and Secretary, Stephan J. Hauser, 1623 Maple Avenue, College Hill, Cincinnati, Ohio. A more complete statement of the meeting will appear in the March issue of THIS JOURNAL. The titles of papers should be sent to the Secretary, Charles L. Parsons, Box 505, Washington, D. C.

The following chairmen of committees have been appointed:

*Executive Committee*, Frederick W. Weissmann.

*Finance Committee*, Archibald Campbell.

*Transportation and Excursions*, Gordon Farnham.

*Press, Publicity and Printing*, C. T. P. Fennel.

*Reception and Registration*, J. W. Ellms.

*Ladies' Reception*, Mrs. J. W. Ellms.

*Entertainment*, Richard Lord.

*Smoker*, F. C. Broeman.

*Banquet*, L. W. Jones.

*Meeting Places*, John Uri Lloyd.

CHAS. L. PARSONS

#### BUREAU OF STANDARDS' ANALYZED SAMPLES

The Bureau of Standards, Washington, D. C., is prepared to issue a sheet brass of the following composition, approximately:

	Per cent	Per cent
Tin.....	1.0	Zinc..... 27.0
Lead.....	1.0	Iron..... 0.3
Copper.....	70.3	Nickel..... 0.5

The fee, payable in advance is \$3.00 per sample of about 150 grams weight.

S. W. STRATTON, *Director*

January 6, 1914

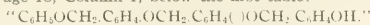
#### SYNTHETIC RESINS—CORRECTION

We note the following errors in our article under the above title, THIS JOURNAL, 6, 3.

(1) Page 8, Column 1, four lines from the end, the equation should read:



(2) Page 10, Column 1, below the first table:



(3) Page 13, Column 2, line nine from the end:

"79 per cent" should read 76 per cent.

L. V. REDMAN

A. J. WEITH

F. P. BROCK

January 21, 1914

#### VEGETABLE OILS EXPORTED FROM CHINA, 1912

The *Oil, Paint and Drug Reporter* states that exports of vegetable oils from China in 1912 amounted to 35,046 net tons of bean oil, 20,281 net tons of peanut oil, and 44,815 tons of wood, tea seed and other oils.

#### ANNUAL TABLES OF CONSTANTS, ETC., VOL. III.

Volume III of the Annual Tables of Constants and Numerical Data, Chemical, Physical and Technological, published by the International Commission of the VIth and VIIth International Congresses of Applied Chemistry is now in press and will be issued in the first half of 1914. A descriptive circular with references to reviews of previous volumes may be secured on application to The University of Chicago Press.

The subscription to Volume III is now opened and will be closed March 31, 1914. The names of subscribers should be sent to The University of Chicago Press, the American agent for the distribution of the Annual Tables. Subscriptions are payable to The University of Chicago Press at the time of publication.

The subscription price of Volume III will be the same as for Volume II, namely, \$6 for the unbound copy, \$6.80 for the



bound copy (carriage free). Members of contributing societies (*The American Chemical Society, The American Electrochemical Society, The Society of Chemical Industry, The American Academy of Arts and Science, the National Academy of Science*) and of contributing manufacturing establishments, are entitled to a discount of 20 per cent (but not on the binding) and will receive the volume unbound for \$4.80, or bound for \$5.60 (carriage free) *provided their subscriptions are received by March 31, 1914.*

After March 31, 1914, the price will be raised to \$6.40 (unbound) and \$7.20 (bound) and a charge will be made for carriage and no discounts allowed.

JULIUS STIEGLITZ, University of Chicago  
EDWARD C. FRANKLIN, Leland Stanford University  
HENRY C. GALE, University of Chicago  
ALBERT P. MATHEWS, University of Chicago  
*Commissioners for the United States*

## PERSONAL NOTES

Prof. Theodore William Richards, of Harvard University, has been elected President of the American Chemical Society for the year 1914. M. T. Bogert and A. D. Little have been elected directors, and C. H. Hertzy, Julius Stieglitz, L. H. Baekeland and W. L. Dudley, councilors-at-large, for a three-year period.

An Anglo-American Exposition to celebrate the centenary of peace and progress in the arts, sciences and industries of the United States and Great Britain, will be held in London, from May to October. A committee has been organized to represent the chemical industries.

Dr. C. E. K. Mees, Director Research Department, Eastman Kodak Company, gave a lecture illustrated with lantern slides, on the problems, equipment and organization for research, in their plant at Kodak Park, Rochester, before the New York Section of the A. C. S., on January 9th, at The Chemists' Club.

Mr. A. K. Comins, formerly in the leather department of A. D. Little, Inc., of Boston, is now with the A. C. Lawrence Leather Company, of Peabody, Mass.

The Wisconsin Section of the A. C. S. met on January 21st. Prof. David Klein gave an illustrated lecture on "Recent Developments in Colloid Chemistry."

Mr. H. E. Howe, of the Bausch & Lomb Company, gave an illustrated lecture on "Optical Glass" and "The Projections of Spectra," before the Western New York Section of the A. C. S. on January 13th.

Sir William Crookes has been elected President of the Royal Society. In view of the invariable practice that the President of the Royal Society should hold no office in similar learned societies at the same time, he has been obliged to resign the Presidency of The Society of Chemical Industry, to which he was elected at the annual meeting in 1913.

Dr. Rudolph Messel was elected President of The Society of Chemical Industry, by the Council, on December 22nd, to complete the unexpired term of Sir William Crookes.

The Philadelphia Section of the A. C. S. held their January meeting on the 22nd. The speakers were Dr. Carl L. Alsberg, Chief of the Bureau of Chemistry; Mr. Charles J. Hexamer, of the Fire Underwriters' Association, who gave an illustrated address on "The Chemistry of Fires, and Chemicals in Fires." Prof. Philip Maas, of the Central High School, exhibited a suite of liquefied gases.

Prof. R. A. Wetzel, of the College of the City of New York, spoke at a recent Colloquium of the General Electric Company Research Laboratory, on the "Relativity Principle," which he illustrated with the models recently described in *Science*.

Mr. Wm. Hoskins and Mr. H'V. Main gave a lecture illustrated with lantern slides, before the Chicago Section of the A. C. S. on January 16th, on "Atmospheric Pollution."

Dr. Reston Stevenson has been promoted to the position of Assistant Professor of Chemistry in the College of the City of New York.

Dr. Wolfgang Ostwald, of the University of Leipzig, Germany, is giving a series of six lectures on colloid-chemistry before various universities and chemical organizations in America, includ-

ing: Columbia, Chicago, Johns Hopkins, Illinois, Cincinnati, Nebraska, McGill (Montreal) Universities, Indianapolis Section of the A. C. S., and others to be arranged later.

The Alabama Section of the A. C. S. was addressed at the January 24th meeting by Prof. B. B. Ross, on "The Occurrence and Composition of Some Alabama Phosphates," and by Prof. C. L. Hare, on "A Study of the Chemical Composition of Cotton Seed."

The International Petroleum Commission of Karlsruhe, Grand Duchy of Baden, Germany, desire to change the Commission into an INTERNATIONAL PETROLEUM INSTITUTE, and have requested the Imperial German Government to submit their plan to the countries represented or interested in the Commission.

Mr. Christian Dantszen and Mr. J. A. Orange, of the General Electric Company Research Laboratory at Schenectady, have recently returned from Europe where they spent three months visiting plants of general interest to the electrotechnical industry.

The Johns Hopkins Medical School has announced the following changes concerning the admission of students: In 1913 the number of students in each class was limited to ninety. In order to receive consideration applications of incoming students must this year be made by July 1st. After that date the various applications will be sifted and the most likely ninety applicants chosen. The requirements for admission in chemistry have been increased so that in addition to the present requirement of 150 hours of laboratory work in inorganic chemistry, an additional 90-100 hours of laboratory work in organic chemistry will be required of all students desiring to enter the school after October, 1914.

Virgil Coblentz, Chief Chemist for Squibb & Co., took the lucky number in a raffle, entitling him to the library and chemical publications of the late William McMurtrie. The drawing was conducted by Dr. Charles Baskerville and was held at The Chemists' Club, New York City, on January 9, 1914.

The Southern California Section of the A. C. S. had as speakers at their meeting on January 16th, Dr. Elbert E. Chandler, of Occidental College, "The Universal Equilibrium," and Mr. H. J. Lucas, of Throop College of Technology, "The Sanitation Service of Porto Rico."

Prof. J. Howard Mathews, of the Chemistry Department of the University of Wisconsin, lectured on "Color Photography," before the Chicago and Indiana Sections of the A. C. S., on December 12th and 13th, respectively, and before the students of De Pauw University on the afternoon of December 12th.

Mr. H. J. Skinner, Vice-President of Arthur D. Little, Inc., Mr. Perry Barker and Mr. Vasco Nunez, of the same organization, spent two weeks in December examining a large industrial plant in Louisiana.

The Cornell, Rochester, Eastern and Western New York and Syracuse Sections of the A. C. S. held a joint meeting at Syracuse University on January 17th. The afternoon program was as follows: "Address of Welcome," Hon. Louis Will, Mayor of Syracuse; "The Use of Physical Measurements in

Chemistry," Dr. C. E. Kenneth Mees, Director Research Laboratories of Eastman Kodak Co.; "Hydrogen Telluride and the Atomic Weight of Tellurium," Dr. Ross P. Anderson of Cornell University; "The Dissociation of Hydrogen into Atoms," Drs. F. Langmuir and G. M. J. MacKay, of the General Electric Company; "The Oxidation of Ammonia to Nitric Acid," Mr. G. N. Terziev, of the Solvay Process Company; "Microscopical Demonstrations with Especial Reference to the Ultramicroscope," Dr. H. C. Cooper, Syracuse University. The evening program included a short organ recital, a brief welcome by Chancellor Day, of Syracuse University and a lecture on "Electrical Energy," by Dr. Charles P. Steinmetz, Professor in Union College and Chief Consulting Engineer of the General Electric Company.

Dr. E. G. Love was tendered a testimonial dinner by the members of The Chemists' Club and their friends, on January 17th, as a mark of appreciation of his long service as Chairman of the House Committee of the Club.

The Eastern New York Section of the A. C. S. held a symposium on "Electronics and Chemistry," at Schenectady, on January 23rd. The symposium was led by Dr. Saul Dushman

with supplementary papers by Messrs. Whitney, Coolidge and Langmuir, of the General Electric Company.

Mr. C. F. Woods, secretary of Arthur D. Little, Inc., presented the Report of the Official Chemists to the American Institute of Metals, at the convention held in Chicago in October. On November 20th, Mr. Woods spoke before the New England Street Railway Club on "The Relation of the Chemist to the Electric Railway."

The Pittsburgh Section of the A. C. S. was addressed on January 22nd by Mr. E. R. Weidlein, of the Mellon Institute of Industrial Research, University of Pittsburgh, on "Adrenaline: Its Nature and Composition."

The Willard Gibbs Medal for 1914 has been awarded by the jury to Doctor Ira Remsen, Past President of the American Chemical Society, and President Emeritus of Johns Hopkins University. This medal was founded by William A. Converse, of Chicago, and is awarded annually by the Chicago Section of the A. C. S. to that chemist who is deemed worthy of recognition because of eminent work in, and original contributions to, pure or applied chemistry.

## BOOK REVIEWS

### Dictionary of Applied Chemistry, revised and enlarged edition.

By SIR EDWARD THORPE and other eminent contributors. Five volumes, 3891 pages. Price per volume, \$13.50; complete set, \$67.50. Longmans, Green & Co., London and New York.

The fourth and fifth volumes of the set have now been issued by the publishers, thus completing the task of thoroughly revising, enlarging and republishing this great work. Volumes I, II, and III were reviewed in *THIS JOURNAL*, 4, 550, 698 and 5, 620.

Vol. IV containing 727 pages covers the subject matter in the usual alphabetical order from Oilstones to Soda. As in previous volumes, the old material has been revised and brought up to date and a number of new subjects have been included, the more important of which are Old Fustic, Olive Oil, Osmium, Oxydases, Industrial Uses of Oxygen and Ozone, Palladium, Palm Oil, Synthetic Perfumes, Phenanthrene, Phytosterol, Pitchblende, Plant Sprays, Polarimetry, Polonium, Potato, Proteins, Ptomaines, Pyrites, Pyrometry, Racemism, Radioactivity, Radium, Refractometer, Refrigeration, Rubber, Saffrole, Salicylic Acid, Saponification, Sewage, Artificial Silk, Smoke Prevention.

In addition to this new material, the other articles show careful revision, correction and extension where the importance of the subject justifies it.

Volume V, 830 pages, treats the subjects beginning with Sodium and ending with Zymurgy. The more important new subjects which have been added to the text are Soils, Solubility, Sulfide Dyes, Synthetic Drugs, Thermite Process, Titanium, Toxins and Antitoxins, Urea and Uric Acid, Vat Dyes and Whiskey; and subjects which have gained in commercial importance since the older edition was published, such as Thorium, Vanadium, Uranium and Tungsten are entirely rewritten and extended.

The revision and publication of these volumes has been a great undertaking and it is gratifying to find that both the editor's work and the mechanical production have been accomplished with such promptness and success. Thorpe's "Dictionary of Applied Chemistry," in its present revised form, is doubtless the most comprehensive and complete book of reference now in existence covering the broad field of Applied Chemistry.

M. C. WHITAKER

### Transactions of the American Institute of Chemical Engineers.

Volume V. (1912) Office of the Secretary, Polytechnic Institute, Brooklyn, N. Y. Published by the Institute through D. Van Nostrand Company, New York, 1913. 8vo., iv + 284 pages.

The Institute held joint meetings with the Eighth International Congress of Applied Chemistry in September, and many of its papers were published in the Congress proceedings, which accounts for the smallness of the present volume.

The frontispiece this year is an excellent photogravure of the Institute's President, Dr. T. B. Wagner. The binding is uniform with the series. This work is either better done or appears to better advantage on the smaller volume. The present volume starts by giving in full the papers which have been read before the Institute, together with the discussions which followed. This throws to the rear of the volume such matter as the Institute's Constitution and membership list. This change in arrangement is an improvement, since the main value of the volume in future years will be the original communications read before the Institute. The Proceedings of the annual meetings have been omitted entirely from this issue. The volume on the whole is a pleasing one and a number of the articles are illustrated. Inspection reveals few errors, although the transcript of the discussions should be edited to give more meaning at times.

The following addresses and papers read before the Institute are contained in the volume:

"Phenol-Formaldehyde Condensation Products," L. H. Baekeland.  
"Protection of Intellectual Property in Relation to Chemical Industry," L. H. Baekeland.

"Notes on a Study of the Temperature Gradients of Setting Portland Cement," Allerton S. Cushman.

"The Production of Available Potash from the Natural Silicates," Allerton S. Cushman and George W. Coggeshall.

"Potash, Silica and Alumina from Feldspar," Edward Hart.

"A Chemical Investigation of Asiatic Rice," Allerton S. Cushman and H. C. Fuller.

"The Beehive Coke Oven Industry of the United States," A. W. Belden.

"Action of Disinfectants on Sugar Solutions," George P. Meade.

"The Decomposition of Linseed Oil during Drying," J. C. Olsen and A. E. Ratner.

"Tests on the Opacity and Hiding Power of Pigments," G. W. Thompson.

"Control of Initial Setting Time of Portland Cement," E. E. Ware.

"The Effect of 'Lime Sulphur' Spray Manufacture on the Eyesight," James R. Withrow.

"Acetylene Solvents," J. H. James.

"The New Chemical Engineering Course and Laboratories at Columbia University," M. C. Whitaker.

"The Need of Standard Specifications in Oils for Paving Block Impregnation," John Haynes Campbell.

"The Presence of Oxygen in Petroleum and Asphalts," Sam. P. Sadler.

"The Chemical Engineer and Industrial Efficiency," Wm. M. Booth.

"Water for Industrial Purposes," Wm. M. Booth.

"The Availability of Blast Furnace Slag as a Material for Building Brick," Albert E. White.

"Technical Accounting and Chemical Control in Sugar Manufacture,"

David L. Davoll, Jr.

"The Bituminous Rocks of the United States and their Use for Street Surfaces," S. F. Peckham.

Code of Ethics.

The diversity of interest shown here gives the assurance that the Institute has not become too highly specialized and indicates well the breadth of Industrial Chemistry and Chemical Engineering.

Special attention might well be called to the address by the retiring President of the Institute, Dr. Leo H. Baekeland, on "Protection of Intellectual Property in Relation to Chemical Industry," as the summing up of an important point of view in the matter of patent reform to which the author and the Institute have devoted much time. In the article on "Acetylene Solvents," Dr. J. H. James, probably the foremost investigator and inventor in this field, has broken his silence and given us some of his results and a hint as to the probable future of acetylene storage. The papers by Wm. M. Booth amply demonstrate the contention of this engineer that the *Chemical Engineer* is probably best fitted for all-round efficiency engineering work. Space is not available for noticing many of the prominent articles, but mention should be made of the excellent and well illustrated article on the new Chemical Engineering Laboratories at Columbia University by Professor Whitaker. He has been fortunate and energetic in securing the means to fulfill the dreams some of us have harbored for years in the matter of university industrial laboratory equipment. The average university industrial chemistry laboratory is equipped only with dreams, although it seems that some do not even believe in the dreams.

Grave doubt might be expressed as to the propriety, in view of the objects of the Institute, in admitting to its publication such an article as "A Chemical Investigation of Asiatic Rice." The investigation is avowedly for the purpose of contributing to the general knowledge of the chemical composition of rice, with an idea of assisting in the problem of "the relation of an exclusive rice diet to the etiology of beri-beri disease." The work is probably a noteworthy one in its field, but if the Institute once lets down the bars so as to admit articles of an analytical nature, or character other than of an industrial manufacturing and engineering one, irrespective of the standing of the authors, its reason for existence is swept away. In discriminating against analytical chemical articles the Institute is in no sense in the position of expressing any idea of degrading analytical chemistry. This branch of chemistry in the eyes of all thinking chemists has always held a position of honor. The present reviewer knows no field of chemistry that calls for more exercise of inventive genius as well as conceded accuracy of thought and manipulation. While Industrial Chemistry and Chemical Engineering are commonly considered the most promising fields for inventive genius, analytical chemistry really offers more frequent opportunity in this direction because of the time element. The confirmation of industrial ideas takes months or years while analytical ones can usually be confirmed or discarded in much more reasonable periods, and the investigator can proceed to other problems. Quite irrespective of all this, analytical chemistry is the faithful handmaid of industrial chemistry and chemical engineering. Many of the most important articles in these fields will contain much analytical data but it will always be secondary, though probably a necessary help, in the solution of the main problem of the paper or investigation. There is ample opportunity for the publication of such articles in other

publications, whether they be researches in analytical chemistry or the analytical chemical investigation of an industrial product. The results of such work are often of the greatest interest to industrial chemists and by industrial chemists I mean manufacturing chemists and chemical engineers. The temptation for any of us to do just such work is often strong and even necessary. The work of drawing the line is, therefore, a difficult one for the officers of the Institute. They are to be congratulated in having so seldom become susceptible to criticism in this regard in the five years of the Institute's existence.

JAMES R. WITHROW

**General Metallurgy.** By H. O. HOFMAN. McGraw-Hill Book Co., Inc. \$6.

Prof. Hofman covers more ground in this book than has been attempted recently in any similar work and has done it uncommonly well. It is what its title indicates and what similar works rarely are, a *general metallurgy*, and treats of the subsidiary branches which are usually slighted or ignored entirely.

The first chapter is very short, merely defining the scope of the work. Then follows a short but adequate chapter on the Properties of Metals. The third chapter is on alloys and is an exceedingly good and clear account of the present theories. It is fully illustrated with diagrams of cooling curves, typical micro-photographs and equilibrium diagrams. There is a curious error on page 59, where it states that in making alloys of copper and zinc "they are charged together in order that the readily fusible metal may dissolve the more refractory," whereas the copper is always melted first and the zinc added, and this is stated as the general process in the preceding sentence.

Chapter IV on Metallic Compounds is arranged in a rather novel method as the grouping is by the acid radicals. This has decided advantages for the purpose of this book.

The chapter on fuels is not as satisfactory as most of the others. A rather disproportionate amount of space is taken up in the description of methods and apparatus that are only of historical interest. As usual, we have long tables of the analyses of picked samples of fuel which, unfortunately, are much better than commercial deliveries. It is difficult to understand the reasons for the selection of the gas producers illustrated; some of those shown have not been exactly brilliant successes, and some of the best are not even mentioned. Prof. Hofman mentions that the depth of a fuel bed must be varied to suit the fuel "and is greater the lighter the fuel." He does not, however, mention that the size of the fuel has more influence in determining the proper depth of bed.

The chapter on Refractory Materials is very good, though perhaps an undue weight is given to composition. An ultimate, or even a "rational" analysis is a very poor guide in the selection of a refractory, as it is much easier to get bricks of good chemical than physical characteristics.

The chapter on Pyro-Metallurgical Processes and Apparatus is excellent. It starts with a rational and useful classification of furnaces and follows this with short descriptions of typical specimens of each: first of those heated by fuel, and then of the electrical. The methods of calculating the efficiency are described and examples given. The various classes of operations, roasting, smelting, refining, etc., are then taken up. Next is the best article on slags the reviewer has seen. They are treated from the point of view of their general similarity to alloys, and the result is excellent.

Wet processes and apparatus follow, and this chapter should be learned by heart by the numerous patentees of such processes who have never worked outside of a laboratory. While Dr. Hofman, of course, recognizes the great value of many of the wet processes, he fully appreciates and explains their disadvantages and difficulties.

Electro Processes and Apparatus come next. The general



principles are well given but no attempt is made to describe special processes.

The eleventh chapter deals with mechanical operations and takes up more than a third of the book. It gives a condensed but clear description of the apparatus and processes of crushing, concentrating and briquetting ore, the mechanical treatment of alloys, handling of liquids, air supply, heating and drying, and, lastly, the purification of gases.

The concluding chapters are on Metallurgical Products and Economic Considerations. Both are very good and it is only a pity the author did not give more on these very important subjects.

Dr. Hofman's long experience in the field and as a teacher has eminently qualified him for the work, and he has produced a book of which he may well be proud, and one that no metallurgist can afford to be without. The bibliography, if alone, would be of the greatest value, and arranged as it is with the references for each subject on the page with the author's text, its usefulness is greatly enhanced.

Unfortunately the publishers have not treated the work as it deserved. The print and illustrations are fair, but the paper and binding are poor and will not stand the use that a book of this character is bound to receive. The proof-reading has been very careless and there are a number of annoying typographical errors. Most of them are obvious and, therefore, not serious, but there are several which make sense but do not convey the author's meaning and are, therefore, liable to mislead those not thoroughly familiar with the subject.

G. C. STONE

**Plantation White Sugar Manufacture.** By W. H. TH. HARLOFF, Manager of the Boedoran Sugar Factory, Java, and H. SCHMIDT, Consulting Sugar Chemist and Engineer, Java. Translated from the second revised Dutch edition, by JAMES P. OGILVIE, F.C.S., Technical Editor of the "International Sugar Journal." Published by Norman Roger, 2, St. Dunstan's Hill, London. Small 8vo. 135 pp., 7s., 6d. net or \$2.00 abroad.

The present translation of Harloff and Schmidt's "Handleitung voor Tropische Witsuikerfabrikatie," is exceedingly opportune. Discussions in technical journals regarding the influence of recent tariff legislation upon white sugar manufacture in the tropics and the growing tendency among cane planters themselves to produce sugars of higher purity indicate that this new treatise is one of the most timely sugar books of the year.

As stated by the authors in their introduction the purposes of the book are (1) to give the reader a practical insight into the most generally adopted methods of preparing white sugar and (2) to present the theoretical side of the subject and give "the reasons just why such and such a procedure and no other must be adopted." The authors very correctly observe that this second subject is of greater importance than the first since it forms the basis for independent thought and research without which all instruction remains a dead letter.

In their discussions of the principles of white sugar manufacture the authors omit, as is proper, all technical descriptions of sulfur-ovens, filter-presses, evaporators, and other equipments of the sugar house. A previous knowledge of such appliances is supposed to have been acquired; the treatise is, therefore, primarily a book for the experienced sugar manufacturer or advanced student and not for the beginner.

The first section of the book deals with the chemistry of white sugar manufacture. This phase of the question is presented clearly and concisely in 25 pages, 10 of which are devoted to the important subject of the coloring substances, derived from the cane or produced during manufacture. The second section of the book discusses the underlying principles of white sugar manufacture as practised upon the plantations of Java; the

scope of this division is indicated by the six headings: Carbonatation, the Acid Thin-juice Process, Raw-juice Sulfitation, Treatment of Thick-juice, Centrifugal Syrup Treatment, and Curing.

The most casual reader will be impressed by the impartiality with which the claims of different processes are discussed. While the authors, for example, admit their preference, on grounds of safety, for double carbonatation, the disadvantages of this method of clarification are stated so fully and the advantages of single carbonatation set forth so fairly that the most partisan advocate of the latter process can find nothing to criticize.

It is to be regretted, however, that in preparing a book for circulation in English-speaking countries a somewhat fuller mention was not made of processes employed outside of Java. In the section, for example, upon raw juice sulfitation, the discussion is limited to the Java procedure, which consists in liming first and then sulfuring. The value of this part would be considerably increased, if the authors had discussed in this connection the merits and demerits of a method employed in the Western Hemisphere in which the sulfuring of the juice precedes the treatment with lime.

The general tone of the book is conservative and in strict agreement with most generally approved results of sugar house experience. Extreme boldness has been a characteristic of several recent departures in sugar-making and a considerable modification of old established principles has resulted. The Kestner evaporator is a practical refutation, if there ever was one, of the orthodox rule that high temperatures must always be avoided in sugar manufacture. A more recent and startling heresy is the Battelle white sugar process in which the raw cane-juice is treated with quicklime, to from 1 per cent to 5 per cent of its weight, and then boiled until all reducing sugars have been destroyed. This process, which has been favorably received in the Hawaiian Islands, is a most glaring violation of an old principle, summarized as follows by Harloff and Schmidt, on page 6 of their new book:

"By the action of lime on glucose at temperatures below 55° C. (131° F.) the chief product is lactic acid, a very stable acid, not subject to spontaneous decomposition, though at higher temperatures glucinic acid and saccharinic acid, with their colored decomposition products, are formed. Since the calcium (lime) salts of acetic acid (lactic acid?) on the contrary, are colorless, during carbonatation, when much lime is present with the glucose, care must be exercised that the temperature remains below 55° C. (131° F.), so long as the liquid is not neutral."

The conservatism of the book makes it, however, an altogether safe one for any manufacturer to follow. In a period when many sugar manufacturers are tending towards a hazardous radicalism the old admonition "Be not too bold!" may have at times a saving influence.

For the information and wealth of suggestions which it offers the book will repay most careful study; it should be read by everyone who is at all interested in sugar manufacture.

C. A. BROWNE

**Metallurgical Analysis.** By NATHANIEL WRIGHT LORD, E.M., late Professor of Metallurgy and Mineralogy, Ohio State University, and DANA J. DEMOREST, B.Sc. in Chemical Engineering, Professor of Metallurgy, Ohio State University. Third edition. McGraw-Hill Book Company, New York. Illustrations 24, pp. xiv + 334. Price, \$2.50 net.

The first edition of this book was issued in 1893 by Prof. Lord, and consisted of notes, written for the use of students in the Metallurgical Laboratory of the Ohio State University. The object was to give, in a condensed form, the series of selected methods in metallurgical analysis which made up the course of study. The second edition appeared in 1903, and the writer endeavored to extend its scope and make it not only a text-book

for students in technical schools, but also a book of reference for young men in metallurgical laboratories. The book was enlarged, due to the treatment of many of the subjects at greater length. The notes were extended and the book was brought up to the state of the science at that time. In this, the third edition, Professor Demorest has rewritten the book, so as to incorporate in the old methods the recent advances in knowledge bearing on them. Many new subjects have been added so as to include practically all the methods of chemical analyses likely to be used by the metallurgical chemist. In so doing, the writer has retained as closely as possible, Professor Lord's method of presentation of the subject. The method of presentation is an admirable one. The chapter usually opens by giving a brief outline of the theories of the method presented, followed by a clear detailed description of the method, giving references where necessary, and closing with a number of very practical notes.

The first chapter of 11 pages is devoted to Preparation of Samples. The second chapter of 9 pages is given to the Analyses of Limestone. Then follow 17 chapters, 160 pages, describing Methods of Analysis for Iron Ores, Iron and Steel, including Methods for Nickel, Vanadium, Tungsten, Chromium, Titanium, Copper, Arsenic, Aluminum, Nitrogen, Oxygen, Hydrogen.

Nine chapters, 52 pages, are devoted to Spelter and Tin Plate Coating, Zinc, Copper, Lead, and Tin in Ores, Analysis of Refined Copper, and Refined Lead, Analyses of Spelter, Brass and Bronze. One chapter, 24 pages, on the Analysis of Coal and Coke. One chapter, 31 pages, on the Analysis of Gases. One chapter, 14 pages, on Clay and other Silicates. One chapter, 5 pages, on Softening of Water for Boiler Use. One chapter, 22 pages, Calculation of Normal Solutions and Tables.

This book is well written. The methods are clear and well defined. It is a pleasure to recommend this book for the purposes as set forth in the caption.

WILLIAM BRADY

#### Review of the Examination of Water and Water Supplies. By

JOHN C. THRESH, D.Sc., M.D., D.P.H. Second edition. P. Blakiston Sons & Company. Philadelphia, Pa. Printed in Great Britain.

This book chiefly aims to be useful in forming an opinion as to the suitability of water supplies for drinking and other domestic purposes. It should not only be helpful to chemists, but to engineers, health officers and others who may be called upon to express an opinion as to the purity of water supplies.

The examination of the waters of rivers, lakes and harbors to determine their capacity for absorbing sewage, the ways in which researches into the purification of water are carried out and field methods of analysis, all questions of considerable importance in America, are scarcely dealt with or are omitted altogether.

Dr. Thresh, who is a practical analyst and medical officer of health of the Essex County Council, England, has written his book from an essentially English standpoint. Where references are made to American and continental practice, they are usually employed by way of illustration and there is little evidence that the procedures employed and recommended have been materially modified by foreign experience. To some analysts in the United States this may prove disappointing, but it is not as a compendium of dry rules of procedure that the book will be most useful.

Dr. Thresh's 600 pages cover a much larger field than do most works on water supplies and to the worker who is conscious of the restrictions which a close observance of American routine imposes, its breadth, liberality of treatment and comprehensiveness should prove inspiring.

The first part of the book describes methods of examining the sources from which water is derived, based on geological and topographical considerations and gives much useful information concerning the environmental study of springs, wells, rivers

and watersheds. The second part describes the objects of analytical methods, physical, chemical, microscopical and bacterioscopic and their interpretation. The third part deals with the apparatus and reagents and the details to be followed in determining the ingredients of water which the author considers are of interest in connection with sanitary and industrial problems and describes methods of calculating and expressing the results. Tables of the results of numerous analyses of waters, typical of English supplies, are included in this part. The appendix describes the preparation of reagents and media.

Departures from present American custom appear in various parts of the book. For example, it is not usual in the United States to taste water which is being examined and, if tasted, it would not at all be likely to be described as mawkish. Nor will American analysts readily recognize the term *sulfur* to indicate deposits. In the determination of free and albuminoid ammonia, American custom is not identical with Dr. Thresh's. The only method of determining nitrates is by reduction, the author giving as his reason for not including others that he has little confidence in them. The determination of the weight of suspended matter, regarded in the United States as of considerable importance in connection with many water supply problems, is not included as an important part of a sanitary analysis.

Notwithstanding its obvious defects which, it should be said, are by no means so important in England as in America, the book should prove a valuable contribution to the library of chemists, health officers and engineers. The author's comments on data and their interpretation are generally notable for their sound, common sense and a generous recognition of the limitations and difficulties of the subject. The book is well printed on good paper and contains numerous illustrations, including 36 plates showing the results of the microscopic examination of sediments. There is no other book in the English language dealing so comprehensively with the subject of the examination of drinking water supplies from the English standpoint.

GEORGE A. SOPER

#### Chemical Technology and Analysis of Oils, Fats and Waxes.

By J. LEWKOWITSCH. Fifth edition, Vol. I. Price, \$6.50. Macmillan & Co., London, and The Macmillan Company, New York, 1913.

In view of the untimely death of Dr. Lewkowitsch at the age of fifty-six while this edition of his monumental work is still in press, a detailed and searching criticism of the present volume would hardly be seemly. Fortunately, there is little to criticize. The volume under review covers the same topics as the corresponding volume of the fourth edition while the size is increased about one-fourth, the present volume comprising 668 pages. This growth is in general the result of a real rewriting of the text as a whole and not merely the introduction of isolated paragraphs of new matter. It is true that in some cases new work is mentioned only very briefly and without substitution of the newer numerical data for the older data which were already tabulated in the earlier editions so that the reader who seeks the actual data of recent work must usually consult the original articles, but this is almost inevitable in so comprehensive a work. It is noticeable that the growth in bulk of the successive editions has not prevented the author from handling his material with that firmness of grasp and logical sequence which has always been a marked feature of this work.

The present volume has a detailed table of contents but no index, an index to the entire work being promised with Volume III. It is greatly to be hoped that, as stated in the technical press, the revision of the entire work will be found to have been completed before the author's death. This fifth edition of "Lewkowitsch" may well stand for many years both as the leading work of reference in its field and as a worthy monument to the professional attainments of its author.

H. C. SHERMAN

# NEW PUBLICATIONS

By D. D. BEROLZHEIMER, Librarian The Chemists' Club, New York

**Analysis: Detection, Determination and Separation of the Chemical Elements. Vol. II.** By A. RUEDISUELE. 8vo. Price, \$6.25. Berne, 1913.

**Analysis, Industrial Organic.** By P. S. ARUP. 8vo., 318 pp. Price, \$2.00. J. & A. Churchill, London.

**Analysis, Quantitative.** By EDWARD G. MAHIN. 8vo. 511 pp. Price, \$3.00. McGraw-Hill Book Co., New York.

**Analysis, Quantitative, in Practice.** By JOHN WADDELL. 8vo. 162 pp. Price, \$1.25. J. & A. Churchill, London.

**Analysis, Qualitative, from the Standpoint of the Ionic Theory.** By WILHELM BOETTGER. 3rd Ed. 8vo. 565 pp. Price, \$3.00. W. Engelmann, Leipzig. (German.)

**Analysis, Text-book of Quantitative Chemical.** By A. C. CUMMINGS AND S. A. KAY. 8vo. 374 pp. Price, \$2.00. Gurney & Jackson, London.

**Bloxam's Chemistry, Inorganic and Organic.** By A. G. BLOXAM AND SAMUEL J. LEWIS. 10th Ed. 8vo. 878 pp. Price, \$5.50. P. Blakiston's Son & Co., Philadelphia.

**Chemistry.** By E. VON MEYER. 8vo. 663 pp. Price, \$4.50. B. Teubner, Leipzig. (German.)

**Chemical, Annual, Van Nostrand's, for 1913.** By JOHN C. OLSEN. 3rd Ed. 8vo. 638 pp. Price, \$2.00. D. Van Nostrand Co., New York.

**Chemical Constitution and Physical Properties.** By S. SMILES. 8vo. 650 pp. Price, \$5.00. Th. Steinkopf, Dresden. (Translation in German.)

**Chemistry in Our Own Times, The Progress of Scientific.** By WILLIAM A. TILDEN. 2nd Ed. 8vo. 366 pp. Price, \$2.00. Longmans, Green & Co., New York.

**Chemische Apparatur (Chemical Machinery and Apparatus).** New Journal. Editor, A. J. KIESER. 4to. Price, \$4.00 per year. Otto Spamer, Leipzig.

**Coal Tar Distillation.** By ARTHUR R. WARNES. 8vo. 200 pp. Price, \$2.00. Gas World, London.

**Essential Oils: Scientific and Industrial Bulletin of Roure Bertrand Fils, Ser. 3, No. 8.** Sm. 8vo. 158 pp. Roure-Bertrand Fils, Grasse.

**Glycerin, Its Production, Use and Determination.** By S. W. KOPPE. 8vo. 196 pp. Price, \$1.25. A. Hartleben, Vienna. (German.)

**Graphite Deposits of Pennsylvania.** By BENJAMIN L. MILLER. 8vo. 147 pp. Topographic and Geologic Survey of Pennsylvania, Report No. 6.

**Loeb, Morris, Scientific Work of.** Edited by THEODORE W. RICHARDS. 8vo. 349 pp. Harvard University Press, Cambridge. Privately printed.

**Metallography. Part II.** By W. GUERTLER. 8vo. 650 pp. Price, \$8.00. Gebrueder Borntraeger, Berlin. (German.)

**Metals, The Microscopic Analyses of.** By FLORIS OSMOND. 3 vols. 2nd Ed. 8vo. 313 pp. Price, \$2.25. Chas. Griffin & Co., London.

**Molybdenum, Vanadium and Tungsten, The Quantitative Methods of Examination of.** By H. MENNICK. L. 8vo. 231 pp. Price, \$2.25. M. Krayn, Berlin. (German.)

**Oils and Fats, Examination of Hydrocarbon.** By D. HOLDE. 8vo. 596 pp. Price, \$6.25. Julius Springer, Berlin. (German.)

**Organic Chemistry. Vol. II.** By JULIUS B. COHEN. 8vo. 427 pp. Price, \$4.00. Edward Arnold, London.

**Quantitative Analysis.** By FRANK CLOWES AND J. BERNARD COLEMAN. 10th Ed. 8vo. 565 pp. Price, \$3.50. P. Blakiston's Son & Co., Philadelphia.

**Rubber and Rubber Planting.** By R. H. LOCK. 8vo. Price, \$1.25. Cambridge University Press, London.

**Sugar Analysis.** By FERDINAND G. WIECHMANN. 3rd Ed. 8vo. 303 pp. Price, \$3.00. John Wiley & Sons, New York.

**Sugar Manufacture.** By SIEGMUND TEITLER. 8vo. Price, \$1.00. Alfred Hoelder, Vienna. (German.)

**Tanning Materials, The.** By J. DEKKER. 8vo. 610 pp. Price, \$5.25. Gebrueder Borntraeger, Berlin. (German.)

**Textiles: Organic and Inorganic Chemistry with Special Consideration of Bleaching, Dyeing and Finishing Processes.** By M. REIMANN. 4th Ed. 8vo. 374 pp. M. Koch, Leipzig. (German.)

**Water, Clean, and How to Get it.** By ALLEN HAZEN. Sm. 8vo. 210 pp. Price, \$1.50. John Wiley & Sons, New York.

**Zinc and Cadmium.** By R. G. M. LIEBIG. 8vo. 598 pp. Price, \$8.00. Otto Spamer, Leipzig. (German.)

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**Alloys and Minerals, The Fractionation of, in the Electric Micro-furnace.** By ARNOLD L. FLETCHER. *Journal of the Chemical Society Transactions*, Vol. 103, 1913, No. 614, pp. 2097-2108.

**Arsenic in Sulfuric and Hydrochloric Acids, Rapid Method for the Determination of.** By H. KOELSCH. *Chemiker Zeitung*, Vol. 38, 1914, No. 1, pp. 5-6.

**Asphalts, Examination of the.** By HEINRICH LOEBELL. *Chemiker Zeitung*, Vol. 38, 1914, No. 2, pp. 18-20.

**Bleaching Methods, Modern Silk.** By HERBERT A. CARTER. *Silk*, Vol. 6, 1913, No. 12, pp. 25-30.

**Catalysis and its Industrial Applications.** By E. JOBLING. *Chemical World*, Vol. 3, 1914, No. 1, pp. 17-19.

**Coal-tar, Naphthalene-free Carbon and the Fractionating Constants of.** By E. C. PAILLER. *Chemical Engineer*, Vol. 18, 1913, No. 6, pp. 221-222.

**Copper Ores, Leaching Shannon.** By FRANCIS S. SCHIMMERA. *Engineering and Mining Journal*, Vol. 96, 1913, No. 24, pp. 1107-1110.

**Essential Oils, Natural and Synthetic (Perfumery).** By JOHN C. UMNEY. *Journal of the Royal Society of Arts*, Vol. 62, 1913, No. 3185, pp. 47-62.

**Ferric Oxid, Some of the Physical Characteristics of.** By W. H. FULWELLER AND A. F. KUNBERGER. *American Gas Light Journal*, Vol. 99, 1913, No. 24, pp. 369-373.

**Fertilizers, The Artificial, and their Significance in Economics.** By KONRAD KUBIERSCHY. *Zeitschrift fuer angewandte Chemie, Aufsatzteil*, Vol. 26, 1913, No. 97, pp. 721-731.

**Flue Dust, Utilization of Blast Furnace.** By EUGENE B. CLARK. *Industrial World*, Vol. 47, 1913, No. 51, pp. 1522-1526.

**Furnace, for High Temperatures, An Electric Vacuum.** By JOHANNES WOLF AND ERICH MUELLER. *Zeitschrift fuer Elektrochemie*, Vol. 20, 1914, No. 1, pp. 1-4.

**Gas: Progress in Carbonization Methods.** By J. H. TAUSSIG, et al. *American Gas Light Journal*, Vol. 100, 1914, No. 1, pp. 2-7 and 10-13.

**Gas: Report Presented by the Committee on Naphthalene Problem of To-day, American Gas Institute.** By H. L. UNDERHILL, et al. *American Gas Light Journal*, Vol. 100, 1914, No. 2, pp. 17-23.

**Iron Blast Furnace, Handling the Raw Materials at the.** By J. E. JOHNSON, JR. *Metallurgical and Chemical Engineering*, Vol. 12, 1914, No. 1, pp. 44-53.

**Metallurgical Practice, Use of Organic Compounds in.** By GEO. PATCHIN. *Chemical World*, Vol. 3, 1914, No. 1, pp. 9-12.

**Methylation Process, A New.** By A. KOETZ AND E. SCHAEFFER. *Journal fuer praktische Chemie*, Vol. 88, 1913, No. 25, pp. 604-640.

**Ore, Concentration of Complex Sulfid, from the Mary Murphy Mine.** By H. C. PARMELEE. *Metallurgical and Chemical Engineering*, Vol. 12, 1914, No. 1, pp. 21-26.

**Ozonator Designs, Notes on Open Up.** By A. VOSMAER. *Metallurgical and Chemical Engineering*, Vol. 12, 1914, No. 1, pp. 36-41.

**Petroleum: Oxidizability of Mineral Oils.** By H. KANTOROWICZ. *Chemiker Zeitung*, Vol. 37, 1913, No. 13, pp. 1594-1595.

**Physical Chemistry, Report on the Progress of, in 1913.** By W. HERZ. *Chemiker Zeitung*, Vol. 38, 1914, No. 3, pp. 25-28.

**Prussic Acid Production by the Dessau Process. The Decomposition of Betain by Caustic Soda.** By FR. ALBUS. *Chemiker Zeitung*, Vol. 37, 1913, No. 149, pp. 1533-1534.

**Rare Earths and their Radioactive By-products; Incandescent Gas Light.** By E. STERN. *Zeitschrift fuer angewandte Chemie, Aufsatzteil*, Vol. 26, 1913, No. 102/3, pp. 806-815.

**Sodium Amalgam and Water, The Interaction of.** By H. B. BAKER AND L. H. PARKER. *Journal of the Chemical Society Transactions*, Vol. 104, 1913, No. 614, pp. 2060-2073.

**Tannins, Vegetable, Further Contributions to the Qualitative Differentiation of.** By E. STASNY. *Journal of the American Leather Chemists' Association*, Vol. 9, 1914, No. 1, pp. 19-25.

**Textiles: The Decortication of Fibrous Plants.** By H. R. CARTER. *Journal of the Textile Institute*, Vol. 4, 1913, No. 2, pp. 231-265.

**Wood, The Action of Chlorin on Pine.** By EMIL HEUSER AND RUDOLF STEBER. *Zeitschrift fuer angewandte Chemie, Aufsatzteil*, Vol. 26, 1913, No. 102/3, pp. 801-806.

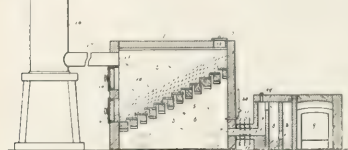
**Wood Oil, Chinese, The Testing of.** By E. W. BOUGHTON. *Drugs, Oils and Paints*, Vol. 29, 1913, No. 7, pp. 252-256.



# RECENT INVENTIONS

By C. L. PARKER, Solicitor of Chemical Patents, McGill Building, Washington, D. C.

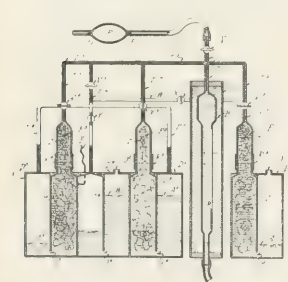
**Preparing Aluminum Sulfate.** H. F. D. Schwahn, Nov. 4, 1913. U. S. Pat. 1,077,309. Clay, shale or other aluminous material is saturated with water and treated with sulfurous acid gas and ozone or ozonized air to transform the aluminum and iron compounds present into sulfate and basic sulfate, respectively. The treated mass is then lixiviated with water, and ozone or ozonized air is injected into the resulting solution until the last trace of iron sulfate therein is transformed into basic ferric salt, which separates as a yellow mud.



The iron-free solution of aluminum sulfate is then drawn off and evaporated.

**Gas-Analyzing Apparatus.** J. W. Hayes, Nov. 4, 1913. U. S. Pat. 1,077,342. This apparatus is designed for the rapid determination of the constituents of furnace gases, illuminating gas, producer gas and the like.

In the use of the apparatus the gas to be analyzed is forced by bulb *P* into measuring burette *B*,



displacing liquid with which it has been previously filled by the use of leveling bottle *L* connected to the burette by tube *R'*. The bottle *L* is then raised until liquid therein reaches the zero mark in burette *B*, whereupon valve *V'* is closed. The gas will then have been measured at atmospheric pressure and at the temperature of the water which surrounds burette *B*. By the operation of the valves in the tubes connected with the neck of the burette the gas may then be forced upon raising the leveling bottle *L*, into the various absorption chambers which may be provided with suitable reagents for the absorption of carbon dioxide, oxygen, carbon monoxid, etc. Each absorption tube is connected at its bottom with a displacement vessel and its top with the neck of the burette.

**Metallizing Ceramic and other Surfaces.** Q. Marino, Nov. 4, 1913. U. S. Pat. 1,077,357. A solution of iron fluoride is applied to the surface to be covered and the iron reduced to a metallic state by applying a finely divided metal capable of reducing the iron.

**Hydrogenizing Organic Compounds.** H. Thorn, Nov. 4, 1913. U. S. Pat. 1,077,442. The substance to be hydrogenized is treated with formic acid and a colloidal solution of a metal of the platinum group.

**Treatment of the Surface of Aluminum Articles.** A. Lang, Nov. 4, 1913. U. S. Pat. 1,077,480. The aluminum surface is coated with a metal chloride and subjected to the action of the heat.

**Boron Nitrid.** R. Heyder, Nov. 4, 1913. U. S. Pat. 1,077,712.

A mixture of boric anhydrid, magnesium and ammonium chlorid is heated to the reaction temperature and after the completion of the reaction, the resulting mixture is washed with a solvent of the by-products of the reaction and the boron nitrid is dried *in vacuo* at a temperature of about 60-70° C.

**Devulcanizing Rubber.** D. A. Cutler, Nov. 11, 1913. U. S. Pat. 1,078,086. The vulcanized rubber is subjected to the action of a bath containing zinc chlorid and oil of pine.

**Hydrogenating Oil Mixtures, Etc.** C. Ellis, Nov. 11, 1913. U. S. Pat. 1,078,136. An acid oil is diluted with a substantially neutral oil and the mixture hydrogenated.

**Extracting Manganese from its Ores.** F. Heusler, Nov. 11, 1913. U. S. Pat. 1,078,199. The manganese ore is first heated to a red heat to calcine a portion thereof. A quantity of the calcined ore is then mixed with a quantity of the crude, uncalcined ore and subjected to a reducing process in the presence of a flux and carbonaceous matter.

**Aluminum Nitrid.** O. Serpek, Nov. 11, 1913. U. S. Pat. 1,078,313. A mixture of carbon and aluminous material is heated to above 1300° C. in a current of nitrogen and hydrogen.

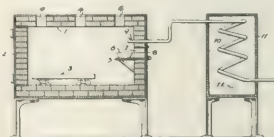
**Recovering Alkalis from Silicate Rocks.** S. Gelléri, Nov. 11, 1913. U. S. Pat. 1,078,495. The silicate rock, mixed with limestone and a sulfate, is heated and the heated mass subjected to the action of ammonium carbonate vapors under high pressure.

**Double Superphosphate.** Wilson and Haff, Nov. 18, 1913. U. S. Pat. 1,078,887. Pyrophosphoric acid is added to natural phosphate rock.

**Metallic Magnesium.** Wallace and Wassmer, Nov. 18, 1913. U. S. Pat. 1,079,079. Magnesium sulfid is gradually added to fused magnesium chlorid and the mixture subjected to electrolysis.

**Sulfur from Hydrogen Sulfid and Sulfur Dioxid.** W. Feld, Nov. 18, 1913. U. S. Pat. 1,079,291. Gases containing sulfuretted hydrogen and sulfurous acid are subjected to the action of a solution of thiosulfate of a metal the sulfid of which is soluble in water.

**Treatment of Iron and Steel for a Permanent Black Finish.** W. R. Swan, Nov. 25, 1913. U. S. Pat. 1,079,453. Articles of iron and steel are placed in the furnace 1 together with a quantity



of copper sulfate, sal-ammoniac or aluminum chlorid, tannin and glucose and heated to about 1050° F. Superheated steam is then injected for about thirty minutes. The iron, after being allowed to cool, is submerged in paraffin oil heated to about 150° F. The treatment gives the treated article a dead black rust-resisting coating.

**White Lead.** E. Euston, Nov. 25, 1913. U. S. Pat. 1,079,481. A substantially neutral lead acetate solution in a tower is sprayed through a constantly renewed atmosphere of carbon dioxide and basic lead acetate solution is introduced at a rate proportional to the precipitation of white lead so as to maintain the lead acetate solution in a substantially neutral condition.

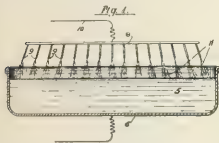
**Concentrating Acid, by means of a Drying Agent.** E. Collett,

Nov. 25, 1913. U. S. Pat. 1,079,541. The acid vapors, such as nitric acid vapors, are introduced through inlet 4 and passed against a counter-current of sulfuric acid, successively through drying columns 1, 2 and 3, escaping into a condenser, 6, from which the concentrated acid is drawn off through pipe 7.

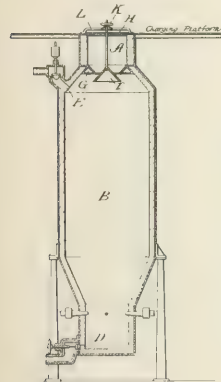
The sulfuric acid is withdrawn from each of the drying columns 1, 2 and 3 and cooled before being introduced into another drying column.

**Bleaching and Thickening Oils and Fats.** O. Scherible, Nov. 25, 1913. U. S. Pat. 1,079,727.

The material to be bleached and thickened is placed in the pan 6, the bottom of which forms one electrode of a high potential current. The other electrode 8, in the form of a lattice with downwardly extending points 9, is arranged above the material which is thus subjected to the action of a silent or brush discharge. The use of a current from 50,000 to 100,000 volts is recommended.

**Zinc Compounds.** E. B. Cutten, Dec. 2, 1913. U. S. Pat. 1,080,102.

Zinc oxide free from slag-forming materials is mixed with coal or coke and heated in a cupola or low blast furnace under a pressure of from 20 to 60 pounds per sq. in. or higher. The heating is effected by means of liquid or gaseous fuel admitted under high pressure to the bottom of the charge. The resulting temperature is sufficient to vaporize the zinc at atmospheric pressure but the pressure maintained in the reducing chamber is sufficient to prevent such vaporization, the zinc being collected as molten metallic zinc.



**Hydrogenation of Organic Compounds, Especially the Fatty Acids, Etc.** K. H. Wimmer, Dec. 9, 1913. U. S. Pat. 1,081,182. Fatty acids and their glycerids are hydrogenated by subjecting them to the action of an organic metal salt and hydrogen.

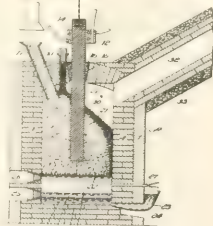
**Electrolytic Manufacture of Perborates.** K. Arndt, Dec. 9, 1913. U. S. Pat. 1,081,191. The perborates are produced by electrolyzing an aqueous solution of borax and sodium carbonate.

**Tungsten and its Alloys.** F. M. Becket, Dec. 16, 1913. U. S. Pat. 1,081,568. Crude ferrotungsten is subjected to an oxidizing roast and the resulting oxides are reduced without substantial fusion of the reduced products. The iron and phosphorus in the reduced product are then removed by an acid treatment.

**Clarifying Wines.** A. Ornstein, Dec. 16, 1913. U. S. Pat. 1,081,623. The flour of ground soya beans (*Soga hispida*), from which the fatty matter has been extracted, is added to the wine to be clarified.

**Electrically Smelting Volatile Metals.** W. M. Johnson, Dec. 9, 1913. U. S. Pat. 1,080,912. This process is primarily intended for reducing and separating zinc from its ores and compounds by a volatilizing process in an electric furnace.

In smelting zinc ores a charge proportioned to yield a fusible slag is superposed upon a molten electrode which may be molten lead, and an electric current passed through the molten electrode, the charge and the evolved zinc vapors. The reduction is carried out in the absence of extraneous air and the volatile reaction products are conducted through the charge and into contact with a portion of such charge heated to the temperature of the maximum reductivity of carbon. The zinc vapors are finally condensed apart from the charge.

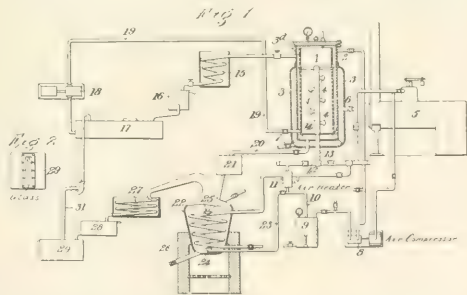


**Acetic Acid.** N. Grünstein, Dec. 23, 1913. U. S. Pat. 1,081,959. Acetic acid is produced from acetaldehyde by the action of oxygen in the presence of acetic acid.

**Waterproof Mortar.** A. Markus, Dec. 23, 1913. U. S. Pat. 1,082,035. A mixture of pulverized soluble soap, pulverized soluble aluminate, lime hydrate and clay is added to the mortar to be waterproofed.

**Vulcanized Glycerol Resin.** W. C. Arsem, Dec. 23, 1913. U. S. Pat. 1,082,106. This is a rubber-like infusible composition comprising a compound of sulfur and the glycerol ester of phthalic and oleic acids.

**Resin and Turpentine from Wood.** C. Howard, Dec. 30, 1913. U. S. Pat. 1,082,526. Chips of coniferous wood are treated with turpentine under pressure to obtain a solution of



the resinous constituents of the wood. The turpentine is agitated during this treatment and the pressure within the treating chamber is caused to alternately rise and fall.

**Fertilizer.** W. E. Carson, Dec. 23, 1913. U. S. Pat. 1,082,108. This is a mixture of pulverized natural limestone and pulverized hydrated caustic magnesium lime.

**Protecting Iron from Rust.** A. Lang, Dec. 23, 1913. U. S. Pat. 1,082,161. A layer of iron oxide is first artificially produced on the surface to be treated and this layer is then chemically combined with an anilin dyeing agent.

**Bituminous Putty.** W. A. Levering, Dec. 30, 1913. U. S. Pat. 1,082,640. The material consists of a major portion of lime dust and a minor portion of air-blown petroleum residuum.

# MARKET REPORT

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR THE MONTH OF JANUARY, 1914

## ORGANIC CHEMICALS

Acetanilid.....	Lb.	21	@	23
Acetic Acid (28 per cent).....	C.	1.62 1/2	@	1.77 1/2
Acetone (drums).....	Lb.	13	@	14
Alcohol, denatured (180 proof).....	Gal.	33	@	36
Alcohol, grain (188 proof).....	Gal.	2.48	@	2.50
Alcohol, wood (95 per cent).....	Gal.	46	@	48
Amyl Acetate.....	Gal.	1.75	to	1.80
Aniline Oil.....	Lb.	10	@	10 1/8
Benzoic Acid.....	Lb.	23	@	27
Benzol (90 per cent).....	Gal.	23	to	25
Camphor (refined in bulk).....	Lb.	40	@	43 1/2
Carbolic Acid (drums).....	Lb.	8	@	10
Carbon Bisulfide.....	Lb.	6 1/2	@	8
Carbon Tetrachloride (drums).....	Lb.	7 1/8	@	7 1/2
Chloroform.....	Lb.	25	@	35
Citric Acid (domestic), crystals.....	Lb.	51	@	52
Dextrine (corn).....	C.	2 02	@	3.13
Dextrine (imported potato).....	Lb.	5	to	6
Ether (U. S. P., 1900).....	Lb.	14	@	20
Formaldehyde.....	Lb.	8 1/2	@	9 1/2
Glycerine (dynamite).....	Lb.	19	@	19 1/2
Oxalic Acid.....	Lb.	7 1/4	@	7 1/2
Pyrogallol Acid (bulk).....	Lb.	1.20	@	1.40
Salicylic Acid.....	Lb.	25	@	30
Starch (cassava).....	Lb.	3 1/4	@	4
Starch (corn).....	C.	2.24	@	2.90
Starch (potato).....	Lb.	4 1/8	—	4 1/4
Starch (rice).....	Lb.	8	@	9
Starch (sago).....	Lb.	2 1/4	@	2 1/4
Starch (wheat).....	Lb.	5 1/4	@	6 1/4
Tannic Acid (commercial).....	Lb.	34	—	35
Tartaric Acid, crystals.....	Lb.	3 11/2	@	3 11/2

## INORGANIC CHEMICALS

Acetate of Lead (brown, broken).....	Lb.	7 1/4	—	7 3/4
Acetate of Lime (gray).....	C.	2.00	@	2.05
Alum (lump).....	C.	1.75	@	2.00
Aluminum Sulfate (high-grade).....	C.	1.25	@	1.75
Ammonium Carbonate, domestic.....	Lb.	8	@	8 1/2
Ammonium Chloride, gray.....	Lb.	5 1/4	@	6 1/4
Aqua Ammonia (drums) 16°.....	Lb.	2 1/4	@	2 1/4
Arsenic, white.....	Lb.	3	@	4
Barium Chloride.....	C.	1.60	@	1.75
Barium Nitrate.....	Lb.	5	to	5 1/4
Barytes (prime white, foreign).....	Ton	19.00	@	23.50
Bleaching Powder (35 per cent).....	C.	1.22 1/2	@	1.30
Blue Vitriol.....	Lb.	5	@	5 1/4
Borax, crystals (bags).....	Lb.	3 3/4	—	4 1/2
Boric Acid, crystals (powd.).....	Lb.	7	—	7 1/2
Brimstone (crude, domestic).....	Ton	22.00	@	22.50
Bromine, bulk.....	Lb.	30	@	35
Calcium Chloride, fused.....	C.	60	@	90
Chalk (light precipitated).....	Lb.	4	@	4 1/2
China Clay (imported).....	Ton	nominal		
Feldspar.....	Ton	8.00	@	12.00
Fuller's Earth, powdered, Foreign.....	Ton	15.00	@	17.00
Green Vitriol (bulk).....	C.	55	@	60
Hydrochloric Acid (18°).....	C.	1.15	@	1.55
Iodine (resublimed).....	Lb.	3.55	@	3.60
Lead Nitrate.....	Lb.	7 1/4	@	8 1/4
Litharge (American).....	Lb.	5 1/4	@	5 1/4
Lithium Carbonate.....	Lb.	65	@	70
Magnesium Carbonate.....	Lb.	21	@	35
Magnesite "Calced".....	Ton	28.50	@	29.50
Nitric Acid, 36°.....	Lb.	3 1/4	@	4 1/4
Phosphoric Acid (sp. gr. 1.75).....	Lb.	2 1/4	@	2 3/4
Phosphorus.....	Lb.	45	@	1.00
Plaster of Paris.....	Bbl.	1.50	@	1.70
Potassium Bichromate, 50°.....	Lb.	6 1/4	@	7
Potassium Bromide.....	Lb.	39	@	40
Potassium Carbonate (calcined), 80 @ 85%.....	C.	3.25	@	3.30
Potassium Chlorate, crystals.....	Lb.	7 1/4	@	7 1/2
Potassium Cyanide (bulk), 98-99%.....	Lb.	16	@	18
Potassium Hydroxide.....	C.	4.00	@	4.25
Potassium Iodide (bulk).....	Lb.	2.95	@	3.00
Potassium Nitrate (crude).....	Lb.	4 1/4	@	5
Potassium Permanganate (bulk).....	Lb.	3 1/4	@	10
Quicksilver, Flask (75 lbs.).....	Lb.	38.00	@	—
Red Lead (American).....	Lb.	6	@	6 1/4
Salt Cake (glass-makers').....	C.	55	@	65

Silver Nitrate.....	Oz.	36 1/2	@	38 1/2
Soapstone in bags.....	Ton	10.00	@	12.00
Soda Ash (48 per cent).....	C.	6 1/2	@	72 1/2
Sodium Acetate.....	Lb.	3 1/2	@	4 1/4
Sodium Bicarbonate (domestic).....	C.	1.00	@	1.10
Sodium Bicarbonate (English).....	Lb.	2 1/2	@	3
Sodium Bichromate.....	Lb.	4 1/2	@	5 1/4
Sodium Carbonate (dry).....	C.	60	@	80
Sodium Chlorate.....	Lb.	7 1/4	@	7 1/2
Sodium Hyposulfite, 60 per cent.....	C.	1.55	@	1.57 1/2
Sodium Hydrosulfide.....	C.	1.30	@	1.60
Sodium Nitrate, 95 per cent, spot.....	C.	—	@	2.22 1/2
Sodium Silicate (liquid).....	C.	65	@	1.50
Strontium Nitrate.....	Lb.	6 1/4	@	7
Sulfur, Flowers (sublimed).....	C.	2.20	@	2.60
Sulfur, Roll.....	C.	1.85	@	2.15
Sulfuric Acid, 60° B.....	C.	85	@	1.00
Talc (American).....	Ton	15.00	@	20.00
Terra Alba (American), No. 1.....	C.	75	@	80
Tin Bichloride (50°).....	Lb.	12 1/2	@	13 1/2
Tin Oxide.....	Lb.	42	@	44
White Lead (American, dry).....	Lb.	5 1/4	@	5 1/2
Zinc Carbonate.....	Lb.	8 1/2	@	9
Zinc Chloride (granulated).....	Lb.	4 1/2	@	5
Zinc Oxide (American process).....	Lb.	5 1/4	@	6 1/4
Zinc Sulfate.....	Lb.	2 1/4	@	3

## OILS, WAXES, ETC.

Beeswax (pure white).....	Lb.	44	@	46
Black Mineral Oil, 29 gravity.....	Gal.	13 1/2	@	14
Castor Oil (No. 3).....	Lb.	8 1/4	@	8 1/4
Ceresin (yellow).....	C.	12	@	22
Corn Oil.....	C.	6.80	@	6.85
Cottonseed Oil (crude), f. o. b. mill.....	Gal.	43	@	45
Cottonseed Oil (p. s. y.).....	Lb.	6.70	@	6.75
Cylinder Oil (light, filtered).....	Gal.	21 1/2	@	32
Japan Wax.....	Lb.	10 1/4	@	10 1/4
Lard Oil (prime winter).....	Gal.	92	@	94
Linseed Oil (raw).....	Gal.	48	@	49
Menhaden Oil (crude).....	Gal.	33	@	37
Neatsfoot Oil (20°).....	Gal.	96	@	98
Paraffine (crude, 120 & 122 m. p.).....	Lb.	3 1/4	@	3 3/4
Paraffine Oil (high viscosity).....	Gal.	26	@	27
Rosin ("P" grade) (280 lbs.).....	Bbl.	4.25	@	4.40
Rosin Oil (first run).....	Gal.	27	@	28
Shellac, T. N.....	Lb.	19	@	19 1/2
Spermaceti (cake).....	Lb.	30	@	35
Sperm Oil (bleached winter), 38°.....	Gal.	72	@	74
Spindle Oil, No. 200.....	Gal.	18	@	19
Stearic Acid (double-pressed).....	Lb.	9	@	12
Tallow (acidless).....	Gal.	65	@	66
Tar Oil (distilled).....	Gal.	30	@	31
Turpentine (spirits of).....	Gal.	47 1/2	@	49

## METALS

Aluminum (No. 1 ingots).....	Lb.	18 1/4	@	18 3/4
Antimony (Hallet's).....	Lb.	7	@	7 1/2
Bismuth (New York).....	Lb.	2.05	@	2.10
Bronze powder.....	Lb.	50	@	3.00
Copper (electrolytic).....	Lb.	14 1/4	@	14 1/2
Copper (lake).....	Lb.	14 1/4	@	14 3/4
Lead, N. Y.....	Lb.	3.95	@	4.07 1/2
Nickel.....	Lb.	50	@	55
Platinum (refined).....	Oz.	43.50	@	44.50
Silver.....	Oz.	57	@	—
Tin.....	C.	37.00	@	—
Zinc.....	C.	5.15	@	5.20

## FERTILIZER MATERIALS

Ammonium Sulfate.....	C.	2	@	2.95 1/2
Blood, dried.....	Unit	3.80	@	—
Bone, 4 1/2 and 50, ground, raw.....	Ton	27.25	@	28.00
Calcium Nitrate (Norwegian).....	C.	2.05	@	2.10
Castor meal.....	Unit	nominal		
Fish Scap, domestic, dried.....	Unit	nominal		
Mowrah meal.....	Ton	nominal		
Phosphate, acid, 16 per cent bulk.....	Ton	—	@	7.00
Phosphate rock, f. o. b. mine.....	Ton	2.75	@	3.00
Florida land pebbles, 68 per cent.....	Ton	5.00	@	5.50
Tennessee, 70-80 per cent.....	Ton	39.07	@	—
Potassium, "murrate," basis 80 per cent.....	Unit	0.13 1/2	@	—
Pyrites, furnace size, imported.....	Unit	3.25 & 10		
Tankage, high-grade.....	Unit	3.25 & 10		



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## TABLE OF CONTENTS

EDITORIALS:	Apparatus for Taking Dust and Bacteria Samples of Air. By Charles Baskerville. . . . .	238
Factors Involved in Opening Up the Field of Unused Elements. . . . .	ADDRESSES:	
182	Recent Developments in Commercial Explosives. E. A. LeSueur. . . . .	239
ORIGINAL PAPERS:	Experiments with Small Animals and Carbon Monoxide. By George A. Burrell and Frank M. Seibert. . . . .	241
Paint Films as Protective Coatings for Concrete. By E. E. Ware and S. M. Schott. . . . .	Chemical Industries and Schools. By Daniel M. Grosh. . . . .	244
184	VENTILATION SYMPOSIUM:	
The Comparative Value of a Calcium Lime and a Magnesium-Calcium Lime for Water Softening. By Edward Bartow and Clarence Scholl. . . . .	Physiological Problems on Ventilation. By Frederic S. Lee. . . . .	245
189	Mechanical Problems of Ventilation. By D. D. Kimball. . . . .	248
Lower Limits of Combustible and Explosive Mixtures of Gases and Air. By E. E. Somermeier. . . . .	Investigation of School Air in New York City. By Charles Baskerville. . . . .	250
191	The New York State Commission of Ventilation and Its Problems. By C.-E. A. Winslow. . . . .	255
A New Method for Determining the Value of Disinfectants. C. A. Duyser and W. K. Lewis. . . . .	CURRENT INDUSTRIAL NEWS:	
198	The Motor Ship "Fionia". . . . .	259
The Lead Contents in Sublimed White Lead—a Calculation. By John A. Schaeffer. . . . .	Boiler Explosions in Chemical Industries in Germany in 1912. . . . .	259
200	Benzol in Germany. . . . .	259
202	Double Scissors Crossing in Rolled Manganese Steel. . . . .	260
The Constitution of White Lead. By Edwin Euston. . . . .	Rubber Statistics. . . . .	260
202	Ancient Norse Iron Nails. . . . .	260
On the Determination of Titanium as Phosphate. By George S. Jamieson and Richard Wrenshall. . . . .	The Chemist in Brazil. . . . .	260
203	Industrial Accidents in 1913. . . . .	261
The Determination of Phenol in the Presence of Hexamethylenetetramine and Formaldehyde. By L. V. Redman, A. J. Weith and F. P. Brock. . . . .	Processes for Fireproofing Wood. . . . .	261
205	German Utilization of Iron-Furnace Slag. . . . .	261
Ultimate Analyses of Coal Tar Pitches. By C. R. Downs. . . . .	Important Process for Purifying Gas from Sugar Compounds. . . . .	262
206	NOTES AND CORRESPONDENCE:	
Note on the Detection of Nickel in Fats. By Robert H. Kerr. . . . .	Synthetic Resins. . . . .	263
207	Valuation of Fluorspar. . . . .	265
Recent Analyses of the Saratoga Mineral Waters. IV. By Leslie Russell Milford. . . . .	Note on the Electrolytic Determination of Copper. . . . .	265
207	Remarks on White Lead Paint Published in 1810. . . . .	266
The Determination of Hardness in Natural Waters. By Clarence Bahlmann. . . . .	On the Decomposition of White Lead Paint. . . . .	266
209	Forty-Ninth Meeting of the American Chemical Society, Cincinnati, April 7-10, 1914. . . . .	266
The Quantitative Estimation of the Salt-soluble Proteins in Wheat Flour. By Geo. A. Olson. . . . .	Note on Certain Unpublished Work on Electrolysis Using Supported Mercury Cathode—A Correction. . . . .	267
211	PERSONAL NOTES. . . . .	267
An Investigation of the Presence of Furfural in Cider Vinegar. By Agnes A. Anderson. . . . .	BOOK REVIEWS:	
214	Treatise on General and Industrial Organic Chemistry; Preservative Coatings for Structural Materials; Die Gerbstoffe-Botanische-chemische Monographie der Tannide. . . . .	268
Some Abnormal Factors of So-called Farmers' Cider Vinegars. By John C. Diggs. . . . .	NEW PUBLICATIONS. . . . .	270
215	RECENT INVENTIONS. . . . .	271
The Analysis of Maple Products. III. The Range of Variation of Analytical Values in Genuine Maple Syrup. By J. F. Snell and J. M. Scott. . . . .	MARKET REPORT. . . . .	272
216		
The Effects of the Ensilage Process on the Solubility of Floats. By E. B. Forbes and Chas. M. Fritz. . . . .		
222		
The Effect of Heat upon the Solubility of the Mineral Constituents of the Soil. By William McGeorge. . . . .		
223		
The Use of Sodium Citrate for the Determination of Reverted Phosphoric Acid. By Alfred W. Bosworth. . . . .		
227		
LABORATORY AND PLANT:		
Applications of Ozone. By A. Vosmaer. . . . .		
229		
A New Viscometer for General Scientific and Technical Purposes. By Eugene C. Bingham. . . . .		
233		
Modified Hempel Pipettes. By R. P. Anderson. . . . .		
237		
An Efficient Method for Cutting Glass. By J. I. Hardy. . . . .		
238		

# EDITORIALS

## FACTORS INVOLVED IN OPENING UP THE FIELD OF UNUSED ELEMENTS<sup>1</sup>

In attempting to classify the accepted elements so that one group, or pseudo-group, contains those elements designated "unused," or "little used," one is confronted with many difficulties. The prime difficulties involve the purpose of the classification and the extent of the use.

Over one-third of the accepted chemical elements have no serious commercial uses at present as elements or compounds. These are given below, classified according to the periodic system for convenience:

ELEMENTS OR COMPOUNDS UNUSED OR LITTLE USED									
0	1	2	3	4	5	6	7	8	Unclas.
He	Rb	Be	Sc	Ge	Cb	Se		Ru	Pr
Ne	Cs	Sr	Y		Yb	Te		Rh	Nd
A			La					Os	Sm
Kr			Ga						Eu
Xe			In						Gd
Nt			Ir						Dy
			Tl						Tm
									Lu
									Tb

About one-half of these have been discovered within the last thirty years. Those so recently made known are usually classified under the two groups of "rare gases" and "rare earths."

Attention is directed to the melting points and specific gravities of four of the rare-earths.

MELTING POINTS	SPECIFIC GRAVITIES
Ce = 623° C.	La = 6.15
La = 810° C.	Pr = 6.48
Nd = 840° C.	Nd = 6.96
Pr = 940° C.	Ce = 7.04
Al = 660° C.	
Ag = 960° C.	

} Given for comparison

Cerium has about the same density as tin (7.3), but all four readily oxidize on exposure to air. Cerium is between lead and tin in its physical appearance, but harder than tin; lanthanum acts much like metallic calcium, its oxide combining readily with water to form the hydroxide, being air slaked, as is lime.

The word "rare" so applied above—as is the case with many words of qualification—has changed its meaning in the light of very recent investigations, although the "rare gases" are found in the atmosphere in the following proportions:

NAME	WT.-%	1 VOL. IN
Helium	4.0	2,450 vols. air
Neon	20.0	808 vols. air
Argon	39.9	105 vols. air
Krypton	81.8	746,000 vols. air
Xenon	128.0	3,846,000 vols. air

Some of the elements mentioned above are by no means so uncommon now and may be had in commercial quantities. Below is a table containing these and some other elements. Many of these have been known for a long time; they are not now used extensively, but invite application.

<sup>1</sup> Author's abstract of an address before the Joint Meeting of the New York Sections of the American Electrochemical Society, the American Chemical Society and the Society of Chemical Industry, at The Chemists' Club, New York, February 6, 1914.

## ELEMENTS NOW AVAILABLE COMMERCIALY BUT LITTLE USED

0	1	2	3	4	5	6	7	8	Unclas.
A	K	Ca	B	Si	As	Se	Br	Co	
		Sr	V	Zr	Cb	Te	I	Pd	
		Ba	La	Ce	Ta				
		Cd		Th					

Now that we have seen the field, let us see what are some of the factors involved in cultivating it. In some cases we lay the lack of use of the elements at once to the scarcity of known occurrences. Haber has shown that osmium is the best catalyst for making ammonia from its elements, but von Welsbach, who devised the osmium-filament lamp, has calculated that there are only a few hundred pounds of osmium available in the periphery of our globe. When, however, we remember that carbon is but 0.21 per cent while silicon is 25.3 per cent of the crust of our earth for a depth of ten miles, including the waters on the earth and its surrounding atmosphere, according to Clarke's calculations, we know that our present utilization of the elements commercially bears but little relation to their total quantity. With some striking exceptions, man has found more or less ample sources of the elements or their compounds when it has been shown that our civilization required them. Tungsten, thorium, vanadium, and radium only need be mentioned in illustration. It is not the small percentage in which these elements occur, for palladium exists in nickeliferous pyrrhotites in quantities too small to be detected by even refined chemical analysis, but it accumulates in the slimes of nickel refineries and is thus obtained in some quantity. The price fixed by possession is the deterrent in the development of the use of palladium, a fact of no individual immorality—quite human perhaps—but contrary to the laws of economics. Some ten years ago one large corporation possessing a store of palladium was approached by some technologists, supported by good repute, with the idea of working out uses for that by-product. The owners said they were not interested in spending a thousand dollars on the investigation—they did not mind spending the money, but they would not be a party to lowering the price of the material in their possession, the inevitable result of extending its use. This principle is well illustrated in the history of metallic aluminum and thorium oxide whose market quotations have fallen to one one-hundredth and two one-hundredths, respectively, what they were one generation ago.

On account of its great resistance to atmospheric oxidation and moisture and to the effect of sulfuretted gases, palladium has been employed for the inner mechanism of chronometers and watches, for the construction of fine balance-beams, for the division scales of delicate apparatus, and for surgical instruments. It has been used for coating silver goods, and for electroplating searchlight mirrors, for soldering platinum, and in dental preparations. Palladized asbestos, palladium sponge and palladium black are most efficient catalytic substances for reducing purposes.

This well known fact may be flashed from the house-tops without any fear of coagulating the clouds of litigation hovering over the oil-hardening situation in this country, as the parties referred to still own the palladium.

Some of these "unused" elements will be used, if the prices are made more reasonable. A very important factor in reducing the market prices of these substances is an improvement in methods of extraction. This may be illustrated in the case of the rare-earths, not with the intention of leading the reader into that maze, but because it shows how modern tools have served the purpose and gives suggestions for needed extension with other elements in that class of "meta-elements," as Crookes termed them.

Monazite sand is essentially a phosphate of the rare earths containing variable amounts of thorium, usually 4-6 per cent. The problem of obtaining thorium compounds from that source—315,000,000 Welsbach mantles was the world's output in 1913—depends upon: (1) Solution, usually by baking, with concentrated sulfuric acid and leaching (very fine grinding of the sand was an essential preliminary); (2) The rare earths and thorium were then thrown out as oxalates to remove the last trace of phosphoric acid; (3) The mixed oxalates were brought into solution with the destruction of the oxalic acid and the thorium precipitated; or, the oxalates were treated with ammonium oxalate, whereby the nonhydrated-thorium-tetra-ammonium oxalate went into solution. This thorium salt was subsequently converted into nitrate. With all this procedure, the price of thorium salts steadily declined until it seemed to reach a limit.

Muthmann and Weiss conceived the plan of distilling off the phosphorus and converting the metallic elements present into carbides. The resultant mass is hard and is very expensive to grind in order subsequently to dissolve it. The writer later produced calcium carbide within the mixture of other carbides, using the unground monazite sand. This mass when thrown into water crumbled at once to a powder from which the suspended milk of lime is readily washed. The residual mass goes into solution in commercial hydrochloric acid from which the thorium may be precipitated at once in a form readily soluble in nitric acid. The cerium may be thrown out of the solution from the thorium precipitate and tons of oxalic acid are not destroyed or locked up in the large quantities of rare-earths accumulated awaiting the development of uses.

Muthmann and Weiss and Hirsch in this country have applied the Hall process for the isolation of metallic cerium, whose use is now practically limited to pyrophoric alloys. The price of metallic cerium in Germany has recently fallen from \$60 to \$5 per kilogram.

Very recently it has been proven to be distinctly profitable, according to separate patents of Soddy and Hahn, to separate meso-thorium compounds in the process of extracting and purifying the thoria. Meso-thorium rivals radium in some of its applications in radio-surgery.

The three instances cited above are given for another

reason. The ideas were worked out by three college professors. Laborers must be provided for clearing the field, whether the toil be that of working out new processes to so reduce the cost of a material as to admit of its application to uses already known to exist, or devise uses not now known for by-products quoted at fictitious prices, but which do not appear at such supposititious values in the annual financial statement.

Undoubtedly the best way to work out problems of the utilization of "undeveloped elements" is to attack them in such well-equipped and splendidly manned research laboratories as are maintained by the General Electric Co., the General Chemical Co., the Eastman Kodak Co., and others, but their upkeep involves large expenditures. Many college and university professors would welcome a subsidy for work of this character, which should be scientific, dignified, and help keep the wolf from the door. We commend for your perusal the amusing "Confessions of a College Professor's Wife," in a recent number of *The Saturday Evening Post*. We do not mean that the college professor is prepared to or should go into the factory, but he can work at an idea, which should later be developed, if it has merit, on a commercial scale by the technical chemist or chemical engineer of the works. Elaboration of this proposition, which is not novel with the speaker, is not necessary here. Suffice it to say that one so selected would bring to the problem a degree of ignorance that might be stimulating and a freedom from tradition which would admit of a display of imagination necessary to utilize material which is commercially abundant.

H. B. Baker has said somewhere, "Nothing can be of more value to science than the exhaustive study of one particular action."

Weiss and Neumann have found that compressed zirconium is a conductor, whereas previous statements have been that it was non-conducting. There is need for reviewing many such statements that are handed down in the literature. Aluminum is sonorous, according to so many text books. Very pure aluminum, such as that used by the late Professor Mallet in the determination of its atomic weight, is not sonorous. If aluminum is sonorous, it is not pure.

Stewart in his charming book on "Recent Advances in Physical and Inorganic Chemistry," in referring to 1887 and the following years of feverish activity in physico-chemical research, led by Arrhenius, van't Hoff and the elder Ostwald, says: "To some extent this wave appears to have spent its force. At the present day physical chemistry, except in the hands of a few exceptional researchers, has degenerated into a means of attacking the problems of pure chemistry instead of opening up new fields; and consequently there is a certain tendency to decry the subject as a mere means to an end, and not a living branch of science. This is, perhaps, an exaggerated view; but it cannot be denied that physical chemists of the present day are not animated by the high hopes which seem to have inspired Ostwald and others in the earlier days of the subject." Bancroft acknowledges that there is some truth in this criticism, but asserts, "The difficulty is that most people are still struggling under the



limitations imposed deliberately and consciously by Ostwald. Once these are broken through, nobody will have any cause to complain of the wave having spent its force." Stewart further says:

"It is an extremely fortunate coincidence that as the first movement declined, a second and perhaps more powerful one had succeeded it. This second movement rose with even greater rapidity than pure physical chemistry, and yet at the present day we appear to have touched only the fringe of the subject of radioactivity; so that we may look forward to a long career of fruitful investigation still before us in this department of chemistry."

The problems of sub-atomic or electronic universe have presented themselves and at once we begin applying these new ideas to utilitarian purposes. The cryogenic laboratories have accumulated fractions from tons of liquefied air. Collie found that the neon, obtained thus incidentally, luminesces under the influence of the Hertzian waves. A tube of neon serves as a detector of the nodes and loops, glowing brilliantly under the influence of the latter, as if it were excited by an induction coil. Claude's tubes of neon thus excited, offer a most pleasing light and perhaps later on will prove to be an economical source of artificial illumination.

Quantities of argon are now available from liquefied air. There are indications that, on account of its inertness, we may shortly see tungsten incandescent lamps, as Whitney puts it, with "the vacuum jam-full of argon" instead of nitrogen.

Troost and Onvrard have stated that they had succeeded in causing argon to combine with magnesium vapor. Neither Rayleigh, Ramsay, nor Moissan were able to secure any evidence of the formation of compounds of argon, however. Many reactions unobserved on the laboratory scale are found to occur when dealing with large quantities of substances, through long periods of time. If this were not true we should have even greater difficulty in accounting for the occurrence of such inert gases as helium in malacome, cleveite and thorionite. It is thus barely possible that in time we shall find compounds of argon produced in the large scale operations of burning the nitrogen of the air, as carried on so successfully in Norway

at present. A use of compounds of argon may then be found.

The development of radioactivity has projected us into an undreamed of realm of thought and new interests. The phenomena of radiology are closely allied to those of radioactivity. The use of Röntgen rays in medicine has been attended by not a few difficulties. Among them the so-called "hardness" and "softness" of the rays. The former are penetrating and affect tissues far below the surface, sometimes favorably and sometimes unfavorably. The "soft" rays affect the epidermis. In the use of "hard" X-rays tubes for deep treatment, it is necessary to screen the skin with various thicknesses of aluminum, or lead, etc. For treatment of skin affections only, there have been no satisfactory means for screening out the penetrating rays, consequently a problem has been the production of "soft" rays with a minimum of "hard" rays. X-ray tube glass is usually a potash or soda-lime silicate. Lindemann found that by substituting lithium for potassium the rays were "softer." He then substituted beryllium for calcium, and finally boron for silicon. Lithium-beryllium-boron-glass shows over thirty per cent reduction in the empirical molecular weight. Windows of this glass let into X-ray tubes give the "soft" rays desired. It would be interesting to see the effect with a potassium-barium-zirconium-glass.

Application of the newer electronic conceptions of valence, especially when associated with residual affinity with the development of methods for changing valence according to our wishes, will unquestionably cause many of these unused elements and many of those now most used to assume new properties. Attention may be directed to one qualitative illustration. Pure lead does not plate on iron. When molten lead is caused to flow to and fro as a conductor of a low-voltage high-amperage alternating current for variable periods of time, usually several hours, it then plates iron, as may be seen from samples very recently so plated under the supervision of the writer. While the process is not perfected, it points a way which may serve as a hint in seeking uses for such elements as cadmium, selenium, and tellurium.

CHARLES BASKERVILLE

## ORIGINAL PAPERS

### PAINT FILMS AS PROTECTIVE COATINGS FOR CONCRETE.

By E. E. WARE AND S. M. SCHOTT

Received December 9, 1913

The extensive use of concrete as a building material for all types of construction has naturally been accompanied by numerous failures of greater or less importance. These examples have been seized upon by manufacturers of competitive material and have been brought to the attention of the public through wide publicity, causing a doubt to arise in the minds of some as to the permanence of concrete construction.

<sup>1</sup> Holder of Paint Fellowship, Acme White Lead and Color Works, 1911-1912.

However, with the better understanding of the possibilities and the limitations of this material, it has been possible to very nearly eliminate the causes of failure that were mainly responsible for the difficulties experienced by the pioneers in the use of concrete construction.

But we are confronted by a cause of disintegration still little appreciated by the concrete engineer—lack of constancy of volume in concrete after setting. Although the tendency to failure from this cause is more apparent in stucco and other light construction, where mixtures rich in cement are used, monolithic work is by no means free from the effects of this lack

of constancy of volume, and we find failure cracks whose presence can be accounted for only by the assumption of a differential expansion in the different members of the structure.

White<sup>1</sup> has shown that the changes in volume due to changes in temperature are small as compared to the changes due to the alternate wetting and drying of the concrete, and that these latter changes are sufficient to cause failure in many cases. Figs. 1 and 2 show representative failure cracks of this type.

Another source of trouble in which water plays a part, is the electrolytic effect of stray currents on the steel reinforcement in concrete. This corrosion of the reinforcement could not take place in perfectly dry concrete.<sup>2</sup> The elimination of these two causes of disintegration in concrete is strictly a problem in waterproofing.

Waterproofing materials for use with concrete are divided into four general classes: membrane, integral, surface washes, and oil paint films.



FIG. 1

Courtesy of Prof. A. H. White

Wig and Bates<sup>3</sup> have made an extensive study of waterproofing materials, and their work seems to show that none of the integral or wash waterproofings are efficient in preventing the absorption of moisture, although they may prevent the percolation of water through the concrete.

Recent work<sup>4</sup> seems to have demonstrated that volume changes are caused by adsorbed water, and that the presence of waterproofing within the concrete has very little effect upon the ultimate percentage change, and that its only effect is to retard the rate of absorption.

The use of an impermeable membrane on the exposed side of the concrete would very efficiently prevent the passage of water to the concrete, and would, therefore, prevent the resultant disintegration due to either moisture, volume changes or to electrolysis. However, in the majority of cases it is not feasible to use an asphalt felt membrane, so we are limited to the

use of the somewhat less efficient but more suitable paint film.

Without doubt paint films can be compounded that will be practically impervious to water; but they must, in the case of concrete coaters, be also able to stand the saponification action of lime leached out from the concrete, as well as be insensitive to the attack of the weather.

Manufacturers have made attempts to solve the problem of putting out a satisfactory concrete coater; but there has been a decided tendency to lose sight of the fact that first of all the paint must be of such a nature as not to lose its elasticity or impermeability through the influence of the weather. The paint must possess all of the weather-resisting qualities of any paint designed for outside work, in addition to being able to meet the conditions peculiar to this particular service.

Concrete coaters may be classified in general: (1) coaters compounded from materials inert to the action

of alkali; (2) coaters whose vehicles carry considerable amounts of free organic acids; (3) coaters compounded with the idea of getting a hard and perfectly impenetrable surface; (4) those coaters whose virtue lies mainly in the elastic and only slightly permeable film formed from the good drying oil which constitutes the major portion of the vehicle.

The first class may contain neutral gum varnishes, petroleum products, may be of a casein base, or may be made up from a cementing pigment.

Experimental data as well as practical experience with paint films for general service work have established the fact that the vehicle for any paint should be selected with a view to getting the maximum of elasticity in the dried film, recognizing that any additions that tend to harden the film will, at the same time, increase the brittleness and accelerate the disintegration.

Paints of the second class are quite common and appeal strongly to the average user, inasmuch as the free acid is supposed to serve the double purpose of neutralizing any lime that may be present and at the same time sealing the pores of the concrete with the

<sup>1</sup> *Proc. Am. Soc. for Test. Mat.*, **1911**.

<sup>2</sup> Rohland, *Wasser u. Abwasser*, **6**, 504. O. Berndt, *Beton u. Eisen*, **11**, 1st Supplement. C. de Wyrall, *Proc. Int. Assn. Test. Mat.*, **2**, 20.

<sup>3</sup> *Bur. Standards, Technologic Paper 3*.

<sup>4</sup> White, Private Communication. Jesser, *Tonind. Ztg.*, **37**, 535-8.

precipitated lime soap. The free acid of this type of paints is sometimes an added fatty acid, and sometimes the unneutralized resin acid of a varnish mixed with the oil as a constituent of the vehicle.

Cathcart<sup>1</sup> claims that the soaps used in water-

No. 2. The same oil to which had been added a small amount of fatty acid.

No. 3. The same oil to which had been added 20 per cent of rosin varnish containing a considerable amount of unneutralized rosin acid.

Each of these samples of oil was shaken at intervals for three weeks, with three different pigments, calcium carbonate, calcium hydrate, and Portland cement. To each of these was added about 10 per cent of water, and the whole was diluted to double its volume with kerosene. A fourth set was shaken with dry Portland cement.

Table I shows that the acid constituents act as completely on Portland cement as they do on calcium hydrate, while they act very slowly on calcium carbonate and unhydrated Portland cement.

Assuming the same conditions to hold under actual conditions of service, there will be an action between the acid of the coater and the cement at the surface of the concrete, which will give a film of lime soap at the surface, to which the paint film must cling. This action is all near the surface, for there is present within one-sixty-fourth inch of the surface of an ordinary concrete sufficient lime compounds to neutralize all the acid content of the common cement coater. These coaters show themselves to be inefficient as neutralizers, and the life of the film cannot be long

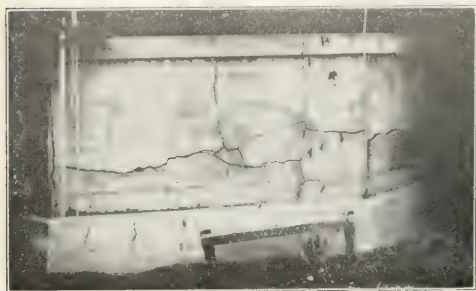


FIG. 2  
Courtesy of Prof. A. H. White

proofing have a disintegrating influence on linoleum. This will apply as well to the insoluble soaps formed in the neutralization of the lime by the free fatty acid of the second type of coater.

In an attempt to determine the extent to which the reactions take place when a coater of this type is

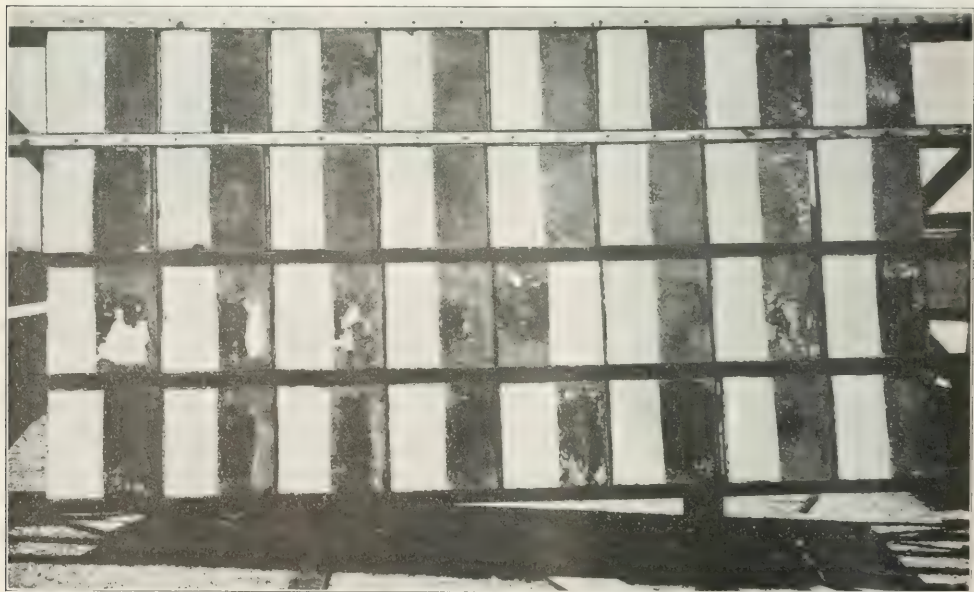


FIG. 3—GROUP OF 32 PANELS, 18" X 18" IN SUPPORTING FRAME. RIGHT HALF OF EACH PANEL PAINTED GREEN

applied to a concrete or stucco surface, some samples of oil were subjected to parallel tests. The oils were as follows:

No. 1. Raw linseed oil.

when they have nothing better with which to bond than a skin of insoluble soap.

The impenetrable surface of the third type of coaters is generally derived from a gum hardened film, the vehicle of this coater being largely varnish.

<sup>1</sup> *Concrete and Const. Eng.*, 7, 380-7.



TABLE I

	LINSEED OIL			OIL AND ACID			OIL AND VARNISH		
	Acid	Sapon.	Iodine	Acid	Sapon.	Iodine	Acid	Sapon.	Iodine
Original.....	1.90	113.0	122.2	9.1	105.5	111.1	6.7	105.4	118.9
Calcium carbonate.....	1.3	118.4	123.3	7.9	109.9	111.9	6.1	110.8	122.8
Calcium hydrate.....	0.1	114.1	122.6	0.2	104.7	114.5	1.2	105.5	125.8
Dry cement.....	1.0	115.6	122.3	4.7	105.0	111.6	2.7	109.4	125.4
Wet cement.....	0.2	114.2	122.6	0.3	105.0	113.2	0.4	103.1	125.6

The tests on iodine absorption were made as a more or less accurate check on the evaporation of the thinner during shaking and centrifuging.

The paints of this class really possess the faults of both the first and the second classes, for the resins of the varnishes are at least in part acid, while as a whole the hard film is subject to the same accelerated disintegrating influences as affect any nonelastic film.

With an idea of studying the efficiency of the different types of coaters, a few of the more widely advertised ones were purchased, and together with some made up in the laboratory, were applied to surfaces of concrete and stucco, and given an exposure test that has extended over about two years time.

The exposure panels were each eighteen inches square and two inches thick, reinforced by expanded metal, and held within a frame built up from  $\frac{1}{4}$  inch x 2 inch steel band, to insure them against breakage. The backs of the panels were covered with galvanized iron in order that there should be no water entering from the back of the panel, and that the conditions should be as nearly as possible the same as those

show cracks, then with the access of water to the underlying concrete and its subsequent evaporation from the surface, lime will be brought to the under surface of the film.

In these tests, each paint was assigned to two panels: one made up from a mix of one part cement to three parts river sand, and one panel of a rich stucco mix, one part lime, two parts cement and five parts river sand. The panels were made up indoors and allowed to set for three weeks before the paints were applied. During the first two weeks of this time the panels were kept damp; but they were allowed to dry a full week in order that there might not be present in the concrete, when the paint was applied, moisture that would prevent proper penetration of the paint and give an imperfect bond between the paint film and the concrete surface. The second coat was applied after the first coat had become thoroughly dry, the time intervening varying from three to seven days.



FIG. 4—PAIR OF PANELS SHOWING COMPLETELY DISINTEGRATED PAINT FILM

existing in an ordinary structure. The paint films were subject, then, to the saponifying action of only such lime as would leach out with the water that might have passed through the film pores, or through cracks that had developed in such films as were unable to stand the weather. If a paint film be water-tight it should be free from the action of lime just so long as it remains in perfect condition; but when it begins to

During the time of exposure, the panels were carried on a frame inclined about  $20^\circ$  from the vertical, with the painted surface of the panel facing south. Fig. 3 shows the complete group of panels with their supporting frame. The frame occupied such a position on the roof of the laboratory as would insure the tests being free from the influence of laboratory fumes.

After having been exposed to the weather for a

period of one year, each panel was coated over one-half of its surface with a green paint whose pigment was a mixture of chrome yellow and prussian blue. This paint served as a very good indicator of the extent to which lime leached out to the surface, the presence of lime being indicated by a yellow spot. In order not to influence the porosity of the underlying film too much, only one coat of the green was applied. In cases where the paint on the panel was disintegrated badly, an attempt was made to prepare the surface for the coat of green paint by brushing off the loosely adhering scales. Even then, in some cases the condition for painting was decidedly unsatisfactory. This emphasizes the importance of using in the first place, a paint which, upon disintegration, will present a proper surface for

closely enough characteristic to warrant a classification according to the type of disintegration. The paints for Panels Nos. 3 and 11 carried, in addition to the fatty acid, a small amount of cement as a constituent of the pigment. While the colloidal silica formed in this way may have been efficient in sealing the pores of the concrete, the fatty acid evidently affected the film, whose early disintegration would not permit these films to be classed as efficient protection for concrete surfaces.

The paints on panels Nos. 6, 14, 17, 18, 19, 20, 21, 22, 31 and 32 depend for their efficiency on the presence of a neutral gum varnish. These panels all exhibited very early disintegration of the coater. This disintegration was, for the most part, characterized by

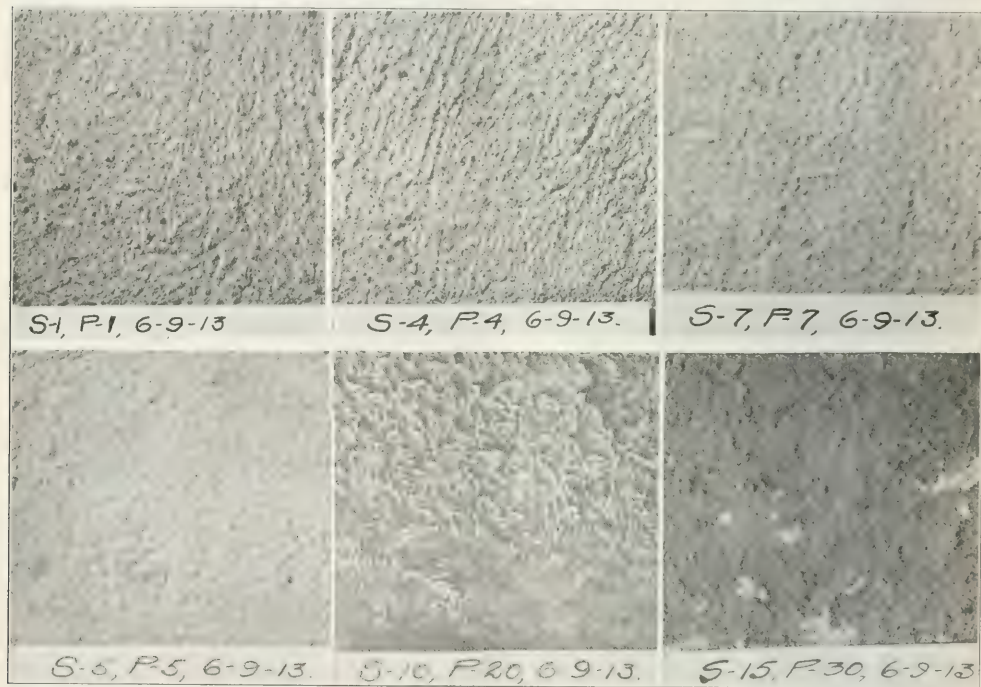


FIG. 5. TYPICAL ILLUSTRATION OF SURFACE CONDITION. ABOUT  $\frac{3}{4}$  SIZE

repainting, for it is a well recognized fact that no paint coat can last indefinitely any more on concrete than on wood or metal. Ladd's<sup>1</sup> work has shown this to be an important consideration in the permanent protection of wooden structures, and the same conditions apply to the protection of concrete.

Table I gives a summary of the condition of the various panels at the end of two years.

Panels Nos. 3, 11, 4, 12, 25 and 26 were painted with coaters carrying considerable amounts of fatty acid or unneutralized resin acid. The disintegration of these films was early and complete, and was not

heavy scaling and flaking, which in some cases left parts of the panel entirely free from paint within a short time.

Coater No. 5, on panels Nos. 5 and 13, was very heavy bodied and did not spread at all freely. The small amount of vehicle present was neutral in character, the material acting more like a cement than a paint, there being little tendency to form a true paint film. These panels retained their coats fairly well, although they at all times showed a high degree of porosity as indicated by the tendency to absorb any water applied to the surface. This coater might serve well as a decorative paint; but it is probably of com-

<sup>1</sup> Bulletins of North Dakota Agricultural Experiment Station.

paratively little value as a protection to the concrete surface upon which it may be applied.

The coaters on panels Nos. 27 and 28 help to prove the contention that non-drying oils do not make good substitutes for linseed oil in paints, for they were among the first to show a tendency to disintegrate.

The vehicles of the paints applied to panels Nos. 1, 2, 7 and 15 were made up very largely of drying oil, the content of varnish being small, and the mineral oils being confined to the thinners. These panels were, to all appearances, the most efficiently protected of any in the test. This is true particularly of panels Nos. 1 and 2, which were prime coated with mild

sensitive to alkali,<sup>1</sup> both sodium hydroxide, and calcium hydroxide attacking it in the cold.

#### SUMMARY

Assuming water to be an important agent in the disintegration of concrete and stucco, there is a necessity for a system of waterproofing that will prevent absorption. The film coaters most nearly fill such a specification, where the surfaces are to be at all ornamental.

No coating compound can be successful that will disintegrate under the influence of the weather. This eliminates from consideration any material that would not be classed as a good coater when applied to other materials than concrete.

Although linoxyn is readily saponifiable in the cold, there is not, under ordinary conditions, enough lime carried out by the small amount of water that may penetrate a paint film in good condition, to cause disintegration of the film. This is emphasized by the fact that the disintegration of the paint film under observation in this work is no more pronounced on a rich lime stucco than on a cement sand concrete.

The absence of stains on the green paint tests in the cases of some of the panels whose coaters showed disintegration at the time of application of the green, would indicate that the lime at the surface of the panels had become pretty well carbonated during the first year. Any stucco exposed to the weather for a year's time can be coated satisfactorily with a good outside paint.

A successful concrete coater should be compounded on the same basis as is used for a satisfactory outside paint for wood, with only such adjustments in composition as tend to make it more nearly impervious, and these must not be made at the expense of the elasticity and general durability of the film.

The panels of these tests are to be repainted with the original materials, and a further set of experiments are in progress in which measurements of the expansion and contraction of the individual panels will be made.

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#### THE COMPARATIVE VALUE OF A CALCIUM LIME AND A MAGNESIUM-CALCIUM LIME FOR WATER SOFTENING

By EDWARD BARTOW and CLARENCE SCHOLL  
Received December 4, 1913

On the market there are limes made from calcium limestones and limes made from magnesium-calcium limestones. The latter is favored by masons because they think it has a smoother plasticity. The claim has been that magnesium-calcium lime is as good as calcium lime for water softening. While we believed that the claim for magnesium-calcium lime was unwarranted, we were glad to make some laboratory experiments to definitely settle the question for ourselves.

We could find but little data concerning the effect of a magnesium-calcium lime for water softening.

<sup>1</sup> Andes, "Drying Oil and Boiled Oil," p. 33.

TABLE II

Coater No.	Panel No.	Amt. ap- plied in grams	Type of Coater	Condition. 2 yrs.	Condition. 1 yr.	Approximate Life	Condition of Green Paint
	(1)	(2)					
1	1	51 64	4	Good	Good	3 yrs.	General Bleaching
1	9	45 45					
2	2	22 39					
2	10	26 36	3	Gone	Very poor	4 mos.	Spotted
3	3	25 43					
3	11	25 42					
4	4	27 43	2	Very poor	Poor	8 mos.	Spotted
4	12	28 38					
5	5	79 68					
5	13	78 70	1	Fair	Good	2 yrs.	Spotted
6	6	61 ..					
6	14	52 ..					
7	7	66 57	4	Fair	Good	2 yrs.	Free from spots
7	15	43 36					
8	8	62 62					
8	16	53 67	3	Gone	Very poor	4 mos.	Few spots
9	17	51 60					
9	18	70 46					
10	19	55 66	1	Gone	Gone	3 mos.	Disintegrated
10	20	48 59					
11	21	63 64					
11	22	48 56	1	Gone	Gone	3 mos.	Disintegrated
12	23	58 50					
12	24	49 45					
13	25	30 ..	2	Gone	Very poor	6 mos.	Few spots
13	26	25 ..					
14	27	27 ..					
14	28	.. ..	1	Gone	Poor	6 mos.	No spots
15	29	48 ..					
15	30	37 ..					
15	31	50 ..	2	Gone	Fair	12 mos.	No spots
16	32	50 ..					
16	31	50 ..					
16	32	50 ..	1	Gone	Very poor	6 mos.	Few spots

process white lead and oil and finished with a special outside white made up of a composite pigment, with the linseed oil vehicle carrying a small amount of varnish as a hardener.

These two panels were subjected to an especially severe test, in that they were exposed at the back during the greater part of the test, the protecting galvanized iron covers having been removed from these particular panels at the end of three months exposure. This permitted water to get in from the back of the panel, which, had the pores of the concrete not been perfectly sealed, would have caused a decided saponification of the linoxyn film, for the water would naturally have evaporated from the side of the panel exposed to the sun, and in this evaporation would have deposited considerable lime within the film. Had the lime come to the surface in any quantities it must have saponified the film, as linoxyn is extremely



We found a record<sup>1</sup> of a sawdust filter impregnated with magnesia used for the removal of calcium salts.

In a paper on the efficiency of lime,<sup>2</sup> Mr. W. F. Monfort states that only the available lime (CaO) should be considered in lime purchasing.

Removal of magnesium from water is mentioned frequently in the literature and a better "flock" is obtained when magnesium is present in solution. This, however, has nothing to do with the effect of magnesium present in lime.

We used for our experiments the water from the University of Illinois water supply. This water is typical of deep drift well waters of central Illinois. An analysis shows that it contains 22 parts per million of carbon dioxide, CO<sub>2</sub>; 128 parts per million of calcium carbonate, CaCO<sub>3</sub>; 90 parts per million of magnesium carbonate, MgCO<sub>3</sub>; and 86.8 parts per million of sodium carbonate, Na<sub>2</sub>CO<sub>3</sub>. Previous experiments<sup>3</sup> have shown that 276 parts per million (equal to 16.0 grains per gallon, 2.3 pounds per thousand gallons) are required to soften the water.

The limes used were furnished by the Ohio and Western Lime Company from their plants at Bedford and Huntington, Indiana. The Bedford lime, the Oxide, is a calcium lime containing very little magnesium. The Huntington limes, one oxide and one hydrate, are magnesium-calcium limes containing a large quantity of magnesium. The analyses of the limes are given below:

THE ANALYSES OF LIMES

Substance	Formula	Calcium lime (Bedford)	Magnesium-Calcium Lime (Huntington)	
			Hydrated Per cent	Oxide Per cent
Calcium oxide.....	CaO	95.60	47.42	53.71
Magnesium oxide.....	MgO	0.84	33.20	37.60
Ferric oxide.....	Fe <sub>2</sub> O <sub>3</sub>	0.02	0.15	0.09
Aluminium oxide.....	Al <sub>2</sub> O <sub>3</sub>	0.85	0.55	0.86
Silica.....	SiO <sub>2</sub>	0.29	0.03	0.00
Carbon dioxide.....	CO <sub>2</sub>	0.18	3.44	0.65
Water.....	H <sub>2</sub> O	2.24	15.20	7.08
Total.....		100.02	99.99	99.99

**METHOD OF PROCEDURE**—A number of portions of water of one liter each were treated with emulsions made from the three limes. The emulsions were of such strength that 1 cc. contained available calcium oxide, equivalent to 5 mg. CaCO<sub>3</sub>. The available calcium oxide was determined by subtracting from the total calcium oxide the amount of calcium oxide necessary to combine with the carbon dioxide, CO<sub>2</sub>, in the lime. Fifteen portions of water were softened to different degrees by adding amounts of the emulsion varying by 10 cc. each from 10 to 150 cc. Two portions were softened by adding amounts less than 10 cc. After adding the emulsion the portions were thoroughly shaken and allowed to stand over night. Each solution after filtration was analyzed. The alkalinity to phenolphthalein and methyl orange, calcium, and magnesium were determined. Results are expressed in terms

of calcium carbonate (CaCO<sub>3</sub>), to simplify calculation. Corrections were made for volume increase due to water added with the emulsion.

A study of the analytical data obtained shows the action of the two limes in softening water. (Compare Tables I and II, and the figure.) All the comparisons are based on the calcium oxide content of the limes. Both limes react first with the free carbon dioxide and

TABLE I—EXPERIMENT WITH CALCIUM LIME  
Results are expressed in parts per million equivalent to CaCO<sub>3</sub>

No.	CaO added	Alkalinity			
		Phenolphthalein	Methyl orange	Calcium	Magnesium
0.....	0	0	332.0	128.8	108.3
1.....	12.5	12.1	342.0	152.7	..
2.....	25	14.1	340.0	141.0	..
3.....	50	14.1	315.1	129.1	123.3
4.....	100	14.3	297.8	102.7	124.5
5.....	150	30.9	263.9	70.5	119.5
6.....	200	41.6	239.2	43.7	116.5
7.....	250	50.4	199.5	29.7	100.0
8.....	300	63.5	197.2	18.1	98.2
9.....	350	66.4	199.0	25.2	96.8
10.....	400	71.1	192.2	31.6	86.3
11.....	450	72.0	163.5	21.4	54.0
12.....	500	70.0	147.4	22.3	38.5
13.....	550	73.3	128.8	22.2	25.1
14.....	600	105.7	141.1	43.6	11.3
15.....	650	138.1	158.2	74.3	12.8
16.....	700	182.8	205.2	140.5	11.5
17.....	750	...	...	178.9	11.0

there is an increase in the calcium content of the water. After the carbon dioxide is used up there is a decrease in the calcium content, the decrease being much more marked in the case of the magnesium calcium lime. While the calcium is more rapidly removed by the magnesium calcium lime, an equivalent of magnesium goes into solution. There is a more rapid decrease in the methyl orange alkalinity when calcium lime is used, the interchanging of calcium for magnesium

TABLE II—EXPERIMENT WITH MAGNESIUM-CALCIUM LIME  
Results are expressed in parts per million equivalent to CaCO<sub>3</sub>

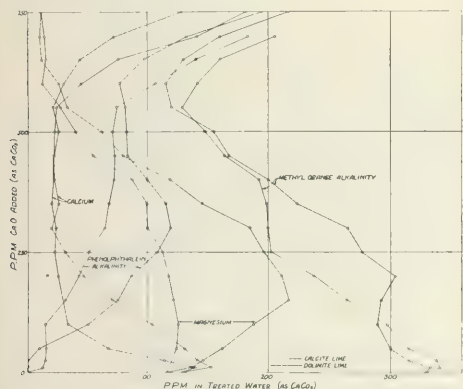
No.	CaO added	Alkalinity			
		Phenolphthalein	Methyl orange	Calcium	Magnesium
0.....	0	0	332.0	128.8	108.3
1.....	12.5	0	335	139.6	138.0
2.....	25.0	0	318	113.9	144.3
3.....	50	8.1	301.0	65.7	160.3
4.....	100	49.0	289.7	34.0	186.0
5.....	150	72.1	292.5	...	216.0
6.....	200	85.3	303.7	24.4	210.3
7.....	250	109.2	277.2	21.1	195.8
8.....	300	118.7	265.0	21.3	184.3
9.....	350	113.4	224.7	17.5	144.8
10.....	400	99.4	200.9	21.3	117.8
11.....	450	80.7	165.7	21.4	79.0
12.....	500	81.4	154.0	25.1	61.0
13.....	550	79.9	119.9	21.1	32.3
14.....	600	76.2	114.2	26.8	29.0
15.....	650	97.2	128.8	42.5	11.5
16.....	700	132.2	159.6	70.9	10.3
17.....	750	193.2	216.2	126.8	10.3

leaving the methyl orange alkalinity nearly constant. The phenolphthalein alkalinity increases more rapidly with the magnesium calcium lime due to the additional magnesium hydrate added. The magnesium reaches a maximum of 216 parts per million (as CaCO<sub>3</sub>) when the calcium content approaches the minimum. The magnesium after reaching a maximum rapidly decreases

<sup>1</sup> *J. Soc. Chem. Ind.*, 1, 176.<sup>2</sup> *Engineering News*, 68, 889.<sup>3</sup> Univ. of Ill., *Bulletin State Water Survey*, Series 7, 98; *Ill. Soc. Eng. & Surv.*, 24, 213.

in amount until the minimum is reached at the point of complete softening. At the point of complete softening the methyl orange alkalinity also reaches the minimum while the phenolphthalein alkalinity is increasing. From the point of maximum softening all the constituents except the magnesium increase. The magnesium does not increase, none being added with the calcium lime and that present in the magnesium-calcium lime is not dissolved.

**SUMMARY**—The difference between the action of calcium and magnesium-calcium limes is that magnesium replaces the calcium until a minimum of calcium carbonate is reached. It also reacts with magnesium acid carbonate forming magnesium carbonate. With the addition of more lime all of the magnesium is precipitated as hydroxide.



WATER SOFTENING BY CALCIUM AND MAGNESIUM—CALCIUM (DOLOMITE) LIME

The softening of water is evidently dependent on the content of available calcium oxide and therefore all lime used for water softening should be bought on the basis of the quantity of available calcium oxide. Moreover, it is not advisable to purchase lime containing magnesium because the magnesium is without value for softening and increases the amount of sludge to be handled.

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## LOWER LIMITS OF COMBUSTIBLE AND EXPLOSIVE MIXTURES OF GASES AND AIR<sup>1</sup>

By E. E. SOMERMEIER

Received Nov. 21, 1913

The prevention of explosions in mines and the successful operation of many industrial and metallurgical processes are to a large degree dependent upon definite information regarding the combustible and explosive properties of mixtures of gases and air. Much of the information on this subject found in the literature is indefinite, contradictory and incomplete or of limited application and the data are so scattered and in such unserviceable form that their proper

correlation, interpretation and application is not at all easy.

It is the purpose of this article to discuss the conditions under which gaseous mixtures may become combustible or explosive, to analyze the various factors which constitute these conditions, to indicate a method for calculating the lower limits of combustible and explosive mixtures and to compare the results of these calculations with existing experimental data. Additional data bearing upon this question will be presented in a subsequent paper.

As a preliminary to the discussion it will be necessary to define with some care the terms which enter largely into the discussion.

### IGNITION TEMPERATURE

(1) The ignition temperature may be defined as the temperature to which a mixture of gas and air or gas and oxygen must be raised in order to produce an appreciably rapid chemical reaction.

(2) The more usual definition of ignition temperature is the temperature to which a portion of a mixture of gas and air or gas and oxygen must be raised in order that chemical reaction may take place throughout the entire gas. This definition implies a self-sustaining reaction and its application is limited to combustible and explosive mixtures. It makes no distinction between the ignition temperature of combustion and the ignition temperature of explosion and on this account it is not adequate. The temperature of ignition of combustion and the temperature of ignition of explosion are two distinct temperatures corresponding to two different reaction velocities and a division into two separate definitions is desirable.

(a) The ignition temperature of combustion is the temperature to which a portion of a gas mixture must be raised in order that combustion may take place and the reaction be propagated throughout the entire mass of gas.

(b) The ignition temperature of explosion is the temperature to which a portion of a gas mixture must be raised in order that an explosion may occur and be propagated throughout the entire mass of gas.

The first definition is of importance as defining the temperature necessary to bring about a reaction. The latter definitions are, however, the ones of practical importance since they are the actual temperatures necessary to produce a combustion or an explosion for a given mixture under a given set of conditions.

### THE IGNITION TEMPERATURES OF COMBUSTION

According to Dixon and Coward,<sup>1</sup> the temperatures to which various gases and air or gases and oxygen must be heated in order to secure ignition when mixed are as follows:

GAS	OXYGEN	AIR
Hydrogen.....	580-590°	580-590°
Carbon monoxide.....	637-658°	644-658°
Methane.....	536-700°	650-750°
Ethane.....	520-630°	520-630°

These values are for a pressure of one atmosphere.

<sup>1</sup> Chem. News, 99 (1909), 139.

<sup>1</sup> Presented in outline to the Columbus Section of the American Chemical Society, January 23, 1913.

Diminishing the pressure of the reacting gases to one-half atmosphere raises the temperature of ignition about 5 degrees. Increasing the pressure 2 atmospheres lowers the ignition temperature by about 30 degrees.

In securing these values the two gases were heated in separate tubes and were then mixed and given an opportunity to react before any appreciable cooling had occurred. Each gas was raised to the same temperature and under these conditions an excess of either one or the other gas caused little difference in the required ignition temperature. The values given include the temperatures of ignition of both rich and poor mixtures of gas with air and with oxygen. As will be seen from the table, carbon monoxide and hydrogen have practically the same ignition temperature with air as with oxygen. These values are the temperatures at which active reaction takes place and correspond to the first definition of ignition temperature. The experiments do not, however, take into account at all whether or not the reaction is self-sustaining and on this account the results do not necessarily represent the actual ignition temperatures of combustible mixtures. They are, however, of value as a basis for the discussion of these temperatures.

#### IGNITION TEMPERATURE OF EXPLOSION

Probably the most reliable values are those given by Falk.<sup>1</sup> These values for ignition temperatures were secured under very high pressures and hence while they probably represent the required ignition temperatures of the explosive wave they do not necessarily express very closely the temperatures necessary to start explosive reactions and originate the high pressure explosive waves. Falk's values for the ignition temperatures of different explosive mixtures of hydrogen and oxygen and of carbon monoxide and oxygen are as follows:

$\text{H}_2 + \text{O}_2 = 314^\circ$	$2\text{CO} + \text{O}_2 = 601^\circ$
$2\text{H}_2 + \text{O}_2 = 540^\circ$	$4\text{CO} + \text{O}_2 = 628^\circ$
$\text{H}_2 + 2\text{O}_2 = 532^\circ$	$\text{CO} + \text{O}_2 = 631^\circ$
$\text{H}_2 + \text{O}_2 + 4\text{N}_2 = 637^\circ$	$2\text{CO} + \text{O}_2 + 2\text{N}_2 = 685^\circ$

These values are for pressures of from 30 to 40 atmospheres. The data were obtained by quick compression of the mixtures to the point where the increase in pressure raised the mixture to a temperature high enough to cause ignition and explosion.

#### DIFFERENCE BETWEEN COMBUSTION AND EXPLOSION

That the temperature of ignition and the temperature of explosion are two separate temperatures corresponding to two different reaction velocities is perhaps best shown by discussing in some detail the difference between combustion and explosion.

During combustion the ignition is communicated direct from molecule to molecule and the zone of combustion spreads as a continuous advancing flame, and if, during the comparatively slow reaction of combustion, the advancing zone of combustion meets an appreciable layer of inert gas the flame is extinguished and combustion ceases. In an explosion the high pressure developed by the initial explosion starts

a detonating or explosive wave which, traveling with great rapidity (in the case of hydrogen 2 miles a second), produces a very high pressure in the gas. The gas being raised to the ignition temperature by this high pressure, ignites and furnishes further energy for continuing the propagation of the explosive wave. During the explosion the ignition may be considered as originating at a great number of separate points along the explosive wave, and if a column of hydrogen and air 2 miles long were to be exploded, the time of the ignition of the portion farthest from the point of origin would be only one second later than that at the origin of the explosion. While a practically continuous mass of igniting gas would exist from end to end of the column, the ignition would not be a continuous propagation from molecule to molecule; and if, in the column of explosive mixture, a layer of inert gas of moderate thickness exists, the explosive wave would pass through this inert gas and the explosion continue on the other side.

The distinction between a violent explosion and a moderate combustion is not difficult to make but the exact line of separation between vigorous combustion and feeble explosion is not so easily drawn. For the same mixture of gas the ignition of a small volume may be clearly a combustion while in the ignition of a larger volume the combustion merges into and becomes an explosion. Assuming the distinction between an explosion and a combustion to be based upon whether the reaction is the continued communication from molecule to molecule or is propagated as an explosive wave due to pressure, there is, at least theoretically, no difficulty in classification. On this basis every explosion is preceded by a more or less brief period of initial combustion.

With a large quantity of gas a combustible mixture is an explosive mixture, since when combustion is once started one of three conditions must result. The reaction decreases in rapidity, is constant, or increases in rapidity. If the rate decreases, the reaction is not self-sustaining and the mixture is not combustible. Under actual conditions a combustion at an exactly constant velocity is not likely to occur; accordingly, any combustible gas will have an accelerated velocity of reaction, and with a considerable amount of gas present an explosion will occur.

#### VELOCITIES OF COMBUSTIBLE AND EXPLOSIVE REACTIONS

If the temperature of ignition of combustion and the temperature of ignition of explosion are clearly recognized as corresponding more or less closely to differences in the velocities of the reactions, it follows that, for any particular mixture of gas with air or with oxygen and under any given set of conditions, there must be a minimum and a maximum rate of velocity of combustion. If the rate of reaction is less than the minimum the gas is incombustible or will not burn under the given conditions. If the rate of reaction reaches or becomes greater than a certain maximum the pressure developed produces a temperature sufficient to start ignition throughout the gas and the combustion becomes an explosion. Just what the velocity of the

<sup>1</sup> Jour. Am. Chem. Soc., 29 (1907), 1536.



reaction will be at any given instant for any given mixture or for any given set of conditions is dependent upon a number of factors, the effects of which will be considered in detail. Some of these factors are as follows:

- (1) The thermal conductivity of the gases.
- (2) The initial temperature of the reacting mixture.
- (3) The initial pressure of the reacting mixture.
- (4) The thermal capacity of the container.
- (5) The amount of excess of either reacting gas over the ratio giving the maximum speed of reaction.
- (6) The amount of inert gases or products of combustion present, such as nitrogen, carbon dioxide, and water vapor.
- (7) The heat of the reaction.
- (8) The volume of the reacting mixture.
- (9) The length of time that the reaction has been in progress.

Nos. 1, 2, 3 and 4 are effective as long as the velocity of the reaction is that of combustion, but during an actual explosion they are of little effect on the ignition temperature of explosion after the explosion is actually under way. They have, however, a very decided effect in aiding or preventing the occurrence of the explosive reaction.

An excess of either gas or the presence of inert gases retards the velocity of reaction and hence raises the ignition temperature whether it be of combustion or of explosion. An increase in the initial temperature of the mixture lessens the radiation and conduction losses and hence lowers the actual temperature required for combustion. In an explosion an increase in the initial temperature of the mixture does not lower the actual ignition temperatures of explosion, but since it lessens the additional heat required to bring about the occurrence of the reaction, it lowers the limit of the amount of combustible gas necessary to be present and makes the gas correspondingly more explosive.

For example, a given mixture of gas of a composition such that at  $0^\circ$  the mixture does not undergo combustion, may, upon an increase in temperature, become not only combustible but actually explosive, because an increase in initial temperature is equivalent to so much more heat generated by the reaction, and may so accelerate the rate of reaction as to change the gas from an incombustible mixture into a combustible and explosive one. On the other hand, a diminished initial temperature increases the conduction and radiation losses and also increases the temperature required for combustion, since with a large radiation and conduction loss the rate of reaction must be accelerated, or the mixture will not support combustion. In an explosion the pressure developed is so high that small differences in the initial pressure are of little effect if an explosion is once started, but a diminished initial pressure may effectively prevent the explosion from beginning since the increased conduction and radiation losses at diminished pressure may prevent a combustion reaction from accelerating into an explosive one.

#### EFFECT OF RADIATION AND CONDUCTION LOSSES

During the initial stage when the speed of combustion is slow, radiation and conduction losses are correspondingly large. For the same temperature conditions the radiation and conduction losses for equal intervals of time may be represented by the spherical surface of the advancing combustion zone, which surface increases with the square of the radius; and if radiation and conduction losses be represented for the first second by  $c$ , for the second second they will be  $4c$ , for the third second  $16c$ , etc. Meanwhile the gas burned, or the total heat generated, is as the cube of the distance the combustion zone has advanced, and at the end of the first second, if it be represented by  $d$ , at the end of the second second it will be  $8d$ , at the end of the third second  $64d$ , etc. From these values, it is apparent that for equal temperature conditions, the radiation and conduction loss, if 50 per cent during the first second, will be only about 25 per cent during the second second and about 12½ per cent during the third second, etc. This diminishing of the percentage of radiation and conduction losses leaves more heat available for further raising the temperature of the reacting gases, and hence for an acceleration of the combustion reactions above the initial rate. This raising of the temperature of the reacting gases above the initial ignition temperature, is accompanied also by increased radiation and conduction losses and the actual percentage decrease of these losses is not quite as rapid as figured above.

#### EFFECT OF PRESSURE ON RATE OF REACTION

A rapid increase in the rate of the combustion reaction is accompanied by an increase in pressure of the reacting gas which in turn further accelerates the rate of reaction. Dixon and Coward<sup>1</sup> show that an increase in pressure from one atmosphere to two atmospheres lowers the required ignition temperature for combustion about  $30^\circ$ , from which, if the temperature of the reacting gases remains the same, doubling the pressure is equivalent in its effect on the rate of combustion reactions to raising the temperature  $30^\circ$ , which as will be shown later corresponds to an eight-fold increase in the rate of reaction.

#### EFFECT OF DUST ON REACTION VELOCITY OR ON IGNITION TEMPERATURE

All gas reactions are accelerated by contact with solids and the effect on the ignition temperature of exceedingly fine dust particles in the gas should be taken into account. It is well known that hydrogen and oxygen in contact with fine palladium will rapidly unite at temperatures below  $100^\circ$  and if extremely fine particles of palladium were to be in suspension throughout a mixture of oxygen and hydrogen, it might be explosive at ordinary temperatures. Very fine dust of any kind has the same effect to a greater or less degree and the effect of dust in coal mines is threefold: (1) The very fine particles may accelerate the ignition reaction and hence lower the temperatures of ignition. (2) The coal particles, being themselves combustible, increase the thermal value of the gas

<sup>1</sup> *Chem. News*, 99 (1909), 139.

and correspondingly less methane or other combustible gas is required to form an explosive mixture. (3) The particles, in being raised to the ignition temperature of the gas, absorb heat and in the case of the coarser dust this absorption of heat may more than counteract any acceleration effect due to surface effect upon the gas reaction. In the case of non-combustible dust as rock dust, the retarding effect may so far exceed the accelerating influence as to render gases less combustible or explosive, while if the dust is exceedingly fine the conditions may be reversed and the mixture may become more explosive. Experimental results by Abel<sup>1</sup> on the effect of fine magnesium oxide upon the explosive properties of mixtures of methane and air showed an appreciable increase in the explosive quality of the gas.

The Explosions in Mines Committee<sup>2</sup> in their third report disagree with Abel's results and state that as the result of an extended series of experiments it found no appreciable effect produced by fine incombustible dust and that the actual effect of the presence of such incombustible dust is to render a gas and air mixture less explosive. Experiments by Dixon and Campbell<sup>3</sup> show errors in Abel's work and their results agree with the Explosion in Mines Committee's report, that the presence of incombustible dust does not make a gas mixture more explosive.

The findings of the Explosion in Mines Committee and the results obtained by Dixon and Campbell apparently disprove Abel's conclusions and indicate that the danger from rock dust has been greatly exaggerated. These experiments, however, do not necessarily disprove the general statement that the presence of exceedingly fine dust particles does accelerate gas reactions and it is entirely possible that their experiments if repeated on gas mixtures containing exceedingly fine dust particles of other kinds might show an increase in explosive properties due to the presence of inert dust. If the dust itself is combustible the increase in the explosive properties of the gas due to the presence of the dust is unquestioned.

#### EFFECT OF INCREASE IN TEMPERATURE ON RATE OF REACTION

According to Ostwald, in many chemical reactions, the rate of reaction is doubled by an increase of  $10^{\circ}$ . If this rate of increase holds true throughout a range of  $100^{\circ}$ , the reaction velocity of a gas having an initial ignition temperature of  $700^{\circ}$ , if raised to  $800^{\circ}$  would increase approximately a thousandfold. The radiation and conduction loss at  $800^{\circ}$  as compared with that at  $700^{\circ}$  is not more than in the ratio of about 5 to 3. Hence, in comparison with the increase in the speed of reaction, the increase in radiation and conduction loss is of minor importance.

The minimum velocities of reaction of combustion and of explosion and the corresponding ignition temperatures of combustion and of explosion, are different for different mixtures and different conditions. The

velocity of combustion must be sufficient to keep the reaction self-sustaining and, since the requirements for being self-sustaining are dependent upon the combined influences of all the factors mentioned, it is evident that the actual velocity and hence the actual ignition temperature are different for every different set of conditions. The maximum velocity of combustion and the ignition temperature corresponding to this velocity are likewise different for each particular set of conditions. The maximum velocity of combustion and the corresponding ignition temperature may be considered as the minimum velocity and the minimum temperature required to produce an explosion. It follows, therefore, that any particular temperature of ignition of combustion and any particular temperature of ignition of explosion can be accurately stated only for some definite mixture under some definite set of conditions.

#### SUMMARY

In order to be adequate, statements regarding the ignition temperature of a gas mixture must be explicit as to whether the temperature of combustion or the temperature of explosion is meant. Also the particular mixture of the gas with oxygen or with air must be stated as well as data as to the presence of inert gases and the initial temperature and the initial pressure.

#### THERMAL REQUIREMENTS FOR COMBUSTION AND EXPLOSION AND THE CALCULATION OF THE COMPOSITIONS OF COMBUSTIBLE AND EXPLOSIVE MIXTURES

While the values for ignition temperatures vary with differences in conditions, the experimental data available are sufficient to serve as the basis for the theoretical calculations of the composition of combustible and explosive mixtures. This calculation involves the heat of combustion, the temperature of ignition and the thermal capacity of the reacting gases. A brief discussion of this last factor is advisable.

#### THERMAL CAPACITY OF GASES

The thermal capacity of a gas for any given temperature range is the amount of heat required to raise it through this range, and is the product of its mean specific heat, the number of degrees of temperature through which it is raised, and the number of unit quantities heated. Tables of thermal capacity afford an easy and ready means for determining the sensible heat contained in the different reacting gases or in the products of combustion for different temperature intervals. The tables may be calculated to any basis desired, as for example the thermal capacity of the gas per gram molecular volume, or the thermal capacity of the gas per gram, or per pound, or the thermal capacity per gram or per pound of one of the constituents.

The thermal capacity of some of the common gases from  $0^{\circ}$  to temperature  $t^{\circ}$  is given in the following table. The values are in small calories per gram molecular volume of gas under constant pressure, and are derived from the general formulas given by Lewis

<sup>1</sup> Report to the Secretary of State for the Home Department, March 23, 1881. For review of this see *Colliery Guardian*, 106 (1913), 812.

<sup>2</sup> *Colliery Guardian*, 106 (1913), 848.

<sup>3</sup> *Jour. Soc. Chem. Ind.*, 32 (1913), 684-687.

and Randall.<sup>1</sup> These formulas are based upon the work of Holborn and Austen, Holborn and Henning and Pier. They are the best data available on the specific heats and thermal capacities of gases.

TABLE OF THERMAL CAPACITIES

Tempera- ture ° C.	O <sub>2</sub> N <sub>2</sub> , CO	H <sub>2</sub>	CO <sub>2</sub> SO <sub>2</sub>	H <sub>2</sub> O	CH <sub>4</sub>	<i>2t</i> calories
0	0000	0000	0000	0000	0000	0000
50	340	338	448	422	504	100
100	682	679	910	843	1038	200
150	1027	1022	1386	1263	1602	300
200	1375	1367	1877	1684	2196	400
250	1725	1715	2380	2104	2820	500
300	2077	2064	2897	2526	3474	600
350	2432	2416	3426	2950	4158	700
400	2789	2770	3966	3377	4872	800
450	3148	3125	4512	3804	5601	900
500	3512	3485	5081	4237	6390	1000
550	3876	3845	5650	4671	7179	1100
600	4243	4209	6239	5112	8028	1200
650	4613	4573	6828	5556	8877	1300
700	4986	4942	7436	6008	9786	1400
750	5360	5311	8043	6462	10695	1500
800	5738	5685	8667	6927	11664	1600
850	6116	6058	9290	7394	12633	1700
900	6501	6436	9929	7875	13662	1800
950	6885	6814	10567	8357	14691	1900
1000	7273	7196	11219	8857	15780	2000

Column 7 gives the value for  $2t$  calories which is the amount by which the thermal value at constant pressure must be diminished to obtain the thermal value at constant volume. For example, the thermal capacity of one molecular volume of air at 600° at constant pressure is 4243. At constant volume it is 4243 — 2(600) or 3043.

#### LIMITS OF COMBUSTIBLE MIXTURES

In calculating the composition of a mixture that will support combustion, the thermal capacity of a mixture should be calculated at constant pressure, since in combustion without explosion the gases have time to expand. In calculating the lower limit of a combustible mixture the heat which must be supplied by the combustion may be considered as equal to the quantity lost by radiation and conduction plus the thermal capacity of the mixture of gas and air at constant pressure when raised from the initial temperature ( $t$ ) to the ignition temperature ( $t'$ ). The higher ( $t$ ) the less the loss due to radiation and conduction at the temperature ( $t'$ ), and hence ( $t'$ ) decreases as ( $t$ ) increases. The difference, ( $t' - t$ ) being smaller, the thermal capacity of the products of combustion is smaller and less combustible gas is required to be present in the mixture. In general, an increase in the initial temperature ( $t$ ) lowers the ignition temperature ( $t'$ ), decreases the difference ( $t' - t$ ), lowers the thermal requirements for combustion conditions and as a result lowers the limit of combustible gas required in order to have a combustible mixture.

#### LIMITS OF EXPLOSIVE MIXTURES

In calculating the composition of an explosive mixture the thermal capacity of the mixture should be taken as at constant volume, since with an explosion traveling at a high velocity the gases have little opportunity to expand. Loss of heat by conduction

is a small factor during an explosion but the quantity of heat generated must be sufficient not only to sustain but to greatly increase the ordinary rate of combustion. For example, in the combustion of a six per cent mixture of methane in air the heat generated by the combustion of the first volume of the mixture is sufficient to heat about three volumes of additional mixture to the ignition temperature of combustion and the heat generated by the combustion of these three volumes is sufficient to raise 9 volumes of mixture to this ignition temperature. The increase being a geometrical one, the rate of the reaction quickly changes the combustion into an explosion.

In an explosive reaction the heat developed by the explosion cannot be less and as a matter of fact considerably exceeds the thermal capacity of the gas or products of combustion heated from the initial temperature ( $t$ ) to the ignition temperature of the explosive mixture ( $t'$ ). In determining the lower limit of an explosive mixture, assuming one volume of mixture, the equation may be written as follows: Heat developed by combustion of  $X$  volume of gas equals the radiation and conduction loss plus the thermal capacity of  $X$  volumes of gas plus  $(1 - X)$  volumes of air from temperature ( $t$ ) to temperature ( $t'$ ),  $X$  being the unknown amount of combustible gas necessary to be present, and  $t'$  the ignition temperature. With radiation and conduction losses quite small and with a known value for  $t'$ , the value of  $X$  is readily calculated.

For example, assuming  $t$  equals 0° and  $t'$ , the temperature of an explosive mixture of methane and air, as 850°, the value of  $X$  is determined as follows:  $X$  molecular volumes of methane on combustion gives  $X(191,200)$  calories. This equals the thermal capacity of  $X$  molecular volumes of methane and  $(1 - X)$  molecular volumes of air from 0 to 850° at constant volume, or  $X(191,200)$  equals  $X(10,933) + (1 - X)(4416)$ . Therefore,  $X = 2.4$  per cent.

Assuming 750° as the ignition temperature of combustion, a 2.4 per cent mixture of methane in air will not support combustion as shown by the following considerations:

0.024 molecular volumes of methane on combustion gives 4589 calories. The thermal capacity of 0.024 molecular volumes of methane plus 0.976 molecular volumes of air from 0 to 750° at constant pressure equals  $0.024(10,695) + 0.976(5,360) = 5488$  calories, or a deficiency in heat of 900 calories. The theoretical amount of methane required for combustion at 750° is calculated as follows:

$X$  molecular volumes of methane on combustion give  $X(191,200)$  calories. This equals the thermal capacity of  $X$  molecular volumes of methane plus  $(1 - X)$  molecular volumes of air from 0 to 750° at constant pressure; or  $X(191,200)$  equals  $X(10,695) + (1 - X)(5360)$ , from which it follows that  $X$  equals 2.9 per cent.

With an initial temperature of 30° (86° F.) about  $\frac{1}{25}$  less of methane will be required or about 2.3 per cent for an explosive mixture and 2.8 per cent for a combustible mixture. The experimental values for

<sup>1</sup> Jour. Am. Chem. Soc., 34 (1912), 1128.



the lower limits of an explosive or combustible mixture of methane and air are usually given as from 5.5 to 6 per cent of methane. Assuming the value 5.5, the excess gas over the calculated amount required for combustion is  $5.5 - 2.8 = 2.7$  per cent, and the excess gas over the calculated amount required for explosion is  $5.5 - 2.3 = 3.2$  per cent. These values indicate that during combustion and for the temperature assumed,  $750^\circ$ , 50 per cent of the heat liberated is available for radiation and conduction losses and for accelerating the reaction; while during an explosion for the temperature assumed,  $850^\circ$ , with radiation and conduction losses practically negligible, nearly 60 per cent of the entire heat liberated is expended in accelerating the reaction or in increasing the pressure of the gas.

#### CALCULATION OF LOWER LIMITS OF COMBUSTIBLE AND EXPLOSIVE MIXTURES OF HYDROGEN AND AIR

Assuming an ignition temperature of  $600^\circ$  the calculation for a combustible mixture is as follows: In one volume of mixture let  $X$  equal the volume of hydrogen and  $1 - X$  the volume of air. Then  $X(58,100)$ , the calories of heat developed, equals the thermal capacity at constant pressure from  $0^\circ$  to  $600^\circ$  of  $X$  volumes of hydrogen plus  $(1 - X)$  volumes of air, which equals  $X(4209) + X(4243)$ . From this it follows that  $X$  equals 7.3 per cent. With an initial temperature of air and gas at  $30^\circ$  ( $86^\circ$  F.) the thermal capacity of the mixture is about  $1/20$  less than this value; therefore,  $1/20$  less of hydrogen or only 6.9 per cent will be required to furnish the necessary heat units.

Assuming an ignition temperature for explosion of  $700^\circ$  C. and neglecting radiation and conduction losses, the lower limit of an explosive mixture of hydrogen and air is obtained by taking the thermal capacity of the gas at constant volume and is found as follows: Let  $X$  equal the hydrogen present in one volume of the mixture; then the heat produced by the combustion of the hydrogen, equals the thermal capacity at constant volume of  $X$  volumes of hydrogen, plus  $1 - X$  volumes of air heated from  $0$  to  $700^\circ$ . In figures this is as follows:

$X(58,100) = X(3,542) + (1 - X)(3,586)$ , in which the value of  $X = 6.2$  per cent.

With an initial temperature of air and gas at  $30^\circ$  the thermal capacity of the mixture is about  $1/25$  less than this value; therefore,  $1/25$  less hydrogen or only 6 per cent will be required to furnish the necessary heat units. The calculated values, 6.9 per cent and 6.0 per cent, are slightly too high, owing to the fact that the thermal capacity of the products of the reaction,  $H_2 + \text{air } (1/2 O + 1.9 N_2) = H_2O + 1.9 N_2$ , is lower than the capacity of the unburned gas, hence after the reaction and after the products have been raised to the temperature of ignition there is a surplus of heat which is available for heating a small additional amount of unburned mixture or for heating the products to a temperature higher than the ignition temperature.

From the table of thermal capacity the capacities

from  $0^\circ$  to  $600^\circ$  before and after the combustion of one molecular volume of hydrogen with oxygen to form water vapor are as follows:

Capacity of unburned gas, $H_2 + 1/2 O_2$	$4209 + 1.9(4243) = 6331$
Capacity of water vapor formed	$= 5112$
Excess	$1219$

This excess (1219 calories) is a little over 2 per cent of the total heat liberated by the combustion of one molecular volume of hydrogen (58,100 calories). Therefore, the calculated values of combustible and explosive mixtures, 6.9 and 6.0 per cent, are correspondingly 2 per cent, or  $1/50$  too high. Making this correction the values are about 6.8 and 5.9 per cent. The thermal calculations on methane and air are subject to a similar correction, which, however, amounts to only 470 calories per molecular volume of methane burned or 191,200 calories, which is less than  $1/4$  per cent of the total heat produced and is more of theoretical interest than of practical importance.

#### TEMPERATURE REQUIRED FOR IGNITION FOR COMBUSTION COMPARED WITH TEMPERATURE REQUIRED FOR IGNITION FOR EXPLOSION

In the foregoing calculations the ignition temperature of combustion for a mixture of hydrogen in air is assumed as  $600^\circ$  and the ignition temperature for combustion for a mixture of methane in air is assumed as  $750^\circ$ . These values are approximately Dixon and Coward's highest values for ignition temperatures, which for hydrogen and air are  $580^\circ$  to  $590^\circ$  and for methane and air  $650^\circ$  to  $750^\circ$ . The ignition temperatures of explosion of hydrogen and air and methane and air are assumed as  $100^\circ$  higher than the ignition temperatures of combustion. These values are not to be regarded as exact but serve merely as a basis of calculation and for discussion of explosive conditions. The value  $700^\circ$  assumed for hydrogen is  $186^\circ$  higher than Falk's value for the ignition temperature of explosion for a 50 per cent mixture of hydrogen in air and  $67^\circ$  higher than his value for the ignition temperature of a 16 per cent mixture of hydrogen in air.

If temperature alone were the cause for the greater rapidity of an initial explosion reaction compared with a combustion reaction, the temperature required to start an explosion necessarily would be very considerably higher than that required to sustain combustion. However, as has been already shown, the high pressure during an explosion is an important factor in producing ignition of the gas at independent points throughout the mass. During combustion the large radiation and conduction losses, which losses are practically absent during an explosion, necessarily raise the actual temperature at which the combustion reaction is self-sustaining considerably above that which would be required if these losses are absent. Taking the influences of these factors into account it is conceivable that the temperature necessary to start and sustain a continuous combustion reaction actually may be as high or higher than the required ignition temperature of an explosion reaction after the explosive wave is once started.

## VALUES OBTAINED BY THERMAL CALCULATIONS COMPARED WITH ACTUAL VALUES

In ordinary combustion, as has already been stated, the products of the reactions are necessarily heated considerably above the temperature actually required to produce the reaction. Otherwise the conduction and radiation of heat to adjacent molecules of unburned gas and air would not be sufficient to raise any of them to the actual combining temperature, and in thermal calculations for combustion where the heat evolved is assumed as equal to the thermal capacity of the reacting gases raised to the ignition temperature, the calculated value for the amount of combustible gas required must be lower than the amount actually required. If on the other hand, the amount of combustible gas actually required to produce an explosive mixture is made the basis of a thermal calculation, the value obtained for ignition temperature of the mixture is higher than the actual temperature required to cause chemical reaction to take place in the mixture. The effect of radiation and conduction losses is to raise the required ignition temperature and to increase the amount of combustible gas required to produce a self-sustaining combustion.

In general, any thermal equation based on the temperature at which two gases will unite if raised to that temperature will give a result for the amount of combustible gas required lower than that which will be obtained experimentally.

Likewise, any thermal equation for combustion which balances if it is based on experimental data actually obtained on gas mixtures that support combustion must give a value for the ignition temperature higher than the temperature at which combustion takes place.

## POTENTIAL EXPLOSIVE PROPERTIES OF GAS MIXTURES

The results of thermal calculations based upon the temperature at which actual chemical reaction takes place fixes the lowest limits of the amount of combustible gas required for a given set of conditions. Any increase in amount of combustible gas over this lower limit or any change of conditions may make the mixture at least potentially combustible or explosive. The theoretical value of 5.9 per cent as the lower limit of an explosive mixture of hydrogen in air and the value of 2.4 per cent as the lower limit of an explosive mixture of methane in air are based on ignition temperatures of  $700^{\circ}$  for hydrogen and  $850^{\circ}$  for methane. Falk's value for the ignition temperature of explosion of a 16 per cent mixture of hydrogen in air is only  $637^{\circ}$ , from which it appears that the assumption of  $700^{\circ}$  as the ignition temperature with approximately a 6 per cent mixture is probably not too low. Natural gas and gas in coal mines frequently contain 10 to 15 per cent ethane which has an ignition temperature of combustion as low as  $520^{\circ}$  and has about twice the heating value of methane volume for volume, which makes a 2 per cent mixture of natural gas at least as explosive as a 2.4 per cent mixture of methane. From these considerations it is apparent that any mixture of over 6 per cent of hydrogen in

air and of over 2 per cent of natural gas with air may be at least potentially explosive.

The results obtained in the laboratory with explosive mixtures are presumably obtained with practically dust-free gas and hence with gas having a high ignition temperature. Furthermore, in laboratory tests the results are usually obtained with mixtures rich enough to ignite and explode without any accelerating influence analogous to blow-out shots, local explosions of rich mixtures, etc.

In mines and factories the mixtures of gas and air are very liable to contain appreciable quantities of fine combustible dust and therefore may have appreciably lower ignition temperatures and be correspondingly more explosive. Any mixture of gas which is potentially explosive is to be regarded as dangerous, as in mines or in other localities there is always the possibility of conditions changing to such an extent that a potential explosion may become an actual one.

## SUMMARY

The data in the literature regarding the explosive properties of gas mixtures are often incomplete and misleading. Definite knowledge is of importance in securing safety in mining and other industrial operations. This knowledge can be made more usable if the various factors bearing upon the question are collected and their effects analyzed.

In order to discuss the problems involved it is desirable to define with some exactness some of the factors and to consider in detail the difference between combustion and explosion.

The ignition temperature of a mixture is the temperature to which it must be raised to bring about an appreciably rapid chemical reaction. Ignition temperature of combustion or explosion is the temperature to which a portion of the mixture must be raised in order that a combustion or an explosion may be propagated throughout the entire mixture. Ignition temperature of combustion and ignition temperature of explosion are two distinct temperatures corresponding to two different reaction velocities. The minimum velocity of a combustion reaction is the lowest velocity at which the combustion is sustained and below which the combustion flame is extinguished. The maximum velocity is the highest velocity for combustion beyond which the reaction becomes explosive. Combustion is produced by direct transfer of energy from molecule to molecule. In an explosion the heat produced by a rapid initial reaction raises the pressure high enough to start an explosion wave, the pressure of which raises the gas to its ignition temperature and the reaction takes place throughout the entire mixture. The exact value for ignition temperature of combustion and for ignition temperature of explosion is affected by changes in initial temperature of the gas, by changes in the initial pressure, and by radiation and conduction losses, and is different for every mixture and for every set of conditions. In order that a gas mixture may support combustion or be explosive the heat produced by the reaction must be more than sufficient to raise the products of combustion and any

inert gases or any excess air present to the ignition temperature of the mixture. Having given the heat of the reaction and the ignition temperature, the calculation of the lower limits of combustible and explosive mixtures of gas is comparatively easy. These theoretical calculations, if based on the temperature at which a reaction will take place, give results for the amounts of combustible gas required lower than the results found by experimental means, as the experimental results necessarily include enough additional combustible gas to overcome the effect of radiation and conduction losses. The values by theoretical calculations while lower than actual values are useful in that they show the potentially explosive properties of a mixture and any potentially explosive gas is to be regarded as dangerous.

Assuming ignition temperatures of combustion of 600 and 750° and ignition temperatures of explosion of 700 and 850° for mixtures of hydrogen in air and of methane in air and determining the amount of each required to satisfy the thermal requirements of the reaction for these temperatures, and assuming combustion as occurring at constant pressure and explosion as occurring at constant volume, the theoretical lower limit of a combustible mixture of hydrogen in air is 6.8 per cent and of methane in air is 2.8 per cent and the theoretical lower limit of an explosive mixture of hydrogen in air is 5.9 and of methane in air is 2.4 per cent.

In a succeeding paper entitled "Partial and Intermittent Combustion of Gas," the writer gives the results of some experiments undertaken in order to obtain further experimental data upon these limits and also to try to harmonize the different experimental values found in the literature, which for air and hydrogen range from 5 to 10 per cent and for air and methane range from 3.2 to 6 per cent.

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#### A NEW METHOD FOR DETERMINING THE VALUE OF DISINFECTANTS

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Since the chief function of a disinfectant is to kill bacteria or other micro-organic growth, its commercial value may be measured in terms of either of two quantities—*first*, the time required for a disinfectant of definite dilution to destroy a predetermined bacterial culture; *second*, that certain dilution necessary to kill the bacteria of this culture in a definite interval of time. But bacteria are living organisms having more or less an individuality. Not only are there many different strains or types of each organism, but the same culture of bacteria may differ in many of its characteristics from day to day. Hence it is impossible to employ as an analytical standard for determining the killing power of disinfectants an organism which may vary in its vitality, or a culture which

may be heterogeneous as to the vitality of the individual bacteria present. The other alternative is to agree upon a certain chemical compound of known composition, and which may be obtained with ease, as the standard disinfectant, and to measure all other disinfectants in terms of the killing power of this standard. Phenol is the substance more generally employed for the purpose, and the ratio of the ability of a disinfectant to kill the bacteria of a certain culture to the ability of phenol to kill the same bacteria under absolutely the identical conditions is called the "Phenol-coefficient."

There are at present three methods for measuring the bactericidal value of disinfectants, all using the above principles, but differing in details of manipulation; these are the Rideal-Walker, the Lancet and the Hygienic Laboratory Methods. Each of these, however, gives unsatisfactory results, not only when carried on by different experimenters in different laboratories, but by the same operators when carrying on his work in duplicate. Blythe<sup>1</sup> has called attention to this fact most forcibly, and has made a strong appeal for a more chemical method for testing disinfecting materials. We believe that the methods now in use are not sound for the following reasons: The mechanism of the reaction by which a disinfectant kills bacteria is not definitely known, but it is generally conceded that the concentration of the disinfecting solution falls in proportion as the number of living bacteria present is decreased. It is possible that the number of molecules of disinfectant is so great in proportion to the number of bacteria present that the change in the concentration of the disinfectant as the living bacteria disappear is negligible. But it is generally true in carrying out these methods that so large a number of bacteria is used that the strength of the disinfectant is materially changed as the killing of the bacteria proceeds and before the last, or more hardy individuals are killed, the disinfectant is appreciably exhausted. Misleading results are therefore obtained.

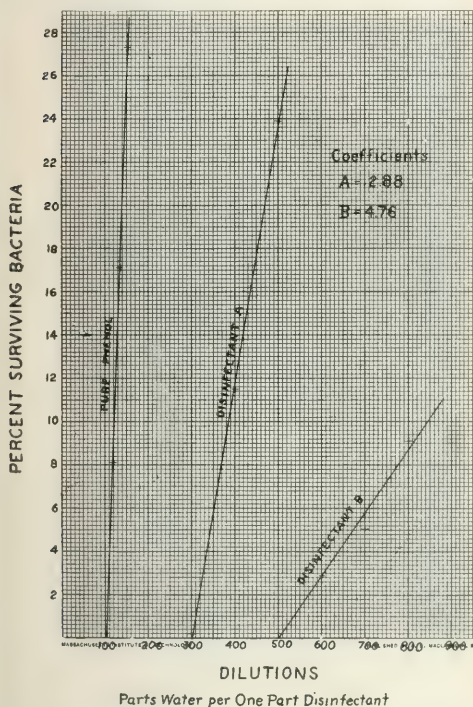
Each of the above methods provides for removing what is supposed to be a perfectly constant volume of the culture from a tube or flask by means of the so-called standard loop. This is a circular loop made by winding a platinum wire of determined size around a rod having a definite diameter. There are so many physical conditions which apparently would influence the volume of liquid such a loop would carry that it was thought of interest to determine this volume. A strong solution of iodine of known strength served as the liquid to be transferred, and a dilute solution of thiosulfate was used to measure the amount of iodine contained in each loopful. A number of loopfuls were withdrawn with great care and placed in cold distilled water. The weight of iodine in each was then determined by titration, and from this data the volume of the loopfuls calculated. When great precautions were used, the volume of one loop varied as much as 30 per cent from the mean of 25 loopfuls, and when hurriedly done the variation rose as high as 80 per cent. The volume transferred by the standard

<sup>1</sup>Orig. Communications, Intern. Cong. Applied Chem., 1909.



loop is on the average 0.003 cc. It may be easily seen that if the number of living bacteria has been largely reduced by the action of the disinfectant it is very possible to transfer a loopful from the disinfected culture to a new culture tube which may contain no living bacteria, even though there are an appreciable number present. But even assuming, notwithstanding the law of chances, that each loopful contains a number of bacteria proportioned to the volume carried by the loop, since this volume may vary by at least 30 per cent from the mean, and may easily vary as much as 80 per cent, concordant results cannot be expected.

The use of a tube of sterile broth into which to transfer the loop of disinfected culture to determine whether



or not all bacteria have been killed, is also unsatisfactory. If the tube should prove fertile there is no means of determining whether the inoculation was due to one stray survivor which happened to be in the loop and whose presence was accidental, or to a considerable number of bacteria which the disinfectant had failed to destroy.

To recapitulate, the present methods are unreliable because: (a) The use of an excessive number of bacteria depletes the disinfecting solution before the culture is rendered sterile. (b) An unknown volume is withdrawn for testing, in that the volume of the standard loop is not constant. (c) It is impossible to determine from the broth tube inoculated, how com-

plete the killing was at the time the sample was withdrawn.

A method developed in this laboratory which seems to eliminate these sources of error, and which is not more laborious, is, in principle, as follows: The disinfectant to be analyzed for its relative bactericidal power is diluted with water to three or four definite concentrations, the extent of dilution depending upon its strength. Pure synthetic phenol is diluted in a like manner. Into a series of these known concentrations of both phenol and the disinfectant under consideration is placed an equal volume of a standard bacteria culture and the mixture allowed to remain an exact number of minutes. At the end of this time an aliquot part of each mixture is plated out in Petri dishes on nutrient agar and incubated until the colonies representing the surviving bacteria can be counted. At the same time plates of equal dilutions of the culture but without the disinfectant are incubated. The ratio of surviving organisms to the number present on the undisinfected plates is then plotted against the dilution, and two curves, one for the standard phenol and one for the disinfectant are obtained. From these the relative strength of the two disinfectants can be read off at any desired point on the curves, and a coefficient either for total killing or any determined percentage of killing may be calculated.

The exact manipulation recommended is as follows: One gram of the disinfectant to be analyzed is weighed accurately and diluted with sterile water to a volume of 100 cc. From this stock solution a series of dilutions is made. Since an equivalent part of each of these is later to be mixed with an equal volume of a dilute water suspension of bacteria, the strength of the series should be twice that of the final dilution desired. When nothing is known of the relative strength of the disinfectant in hand, dilutions of one part disinfectant in 200, 400, and 800 parts sterile water have been found advisable. From a 5 per cent solution of synthetic phenol a series of dilutions of one part phenol to 100, 125 and 150 parts water will give a curve covering a considerable range of killing when *B. coli communior* is used. Tubes of sterile broth and nutrient agar culture medium are prepared according to the standard methods, and a number of 10 cc. and 1 cc. pipettes and ordinary test tubes are provided.

Ten cc. of each of the dilutions of disinfectant and phenol are added to properly marked test tubes and placed in a water bath at 20° C. Ten cc. of a broth culture of *B. coli*, so diluted with sterile water that 1 cc. contains from 20,000 to 60,000 bacteria, are placed by means of a straight graduated pipette in test tubes, one more than the number of disinfectant and phenol tubes just described, and these are also placed in the water bath. This is a twenty-four hour broth culture of reaction +1, which has been transformed daily for not less than three days. When the whole has come to a temperature of 20° C. the contents of one of the tubes of disinfectant is poured into one of the tubes of bacteria and well shaken. After one-half minute this procedure is repeated with the second tube and so on through the series. At the end of five

minutes, 1 cc. is withdrawn from the first tube of disinfected bacteria and added to a bottle containing 99 cc. of sterile water; one-half minute later the second tube is so treated and the others at  $\frac{1}{2}$  minute intervals in the same way. To the tube of bacteria in which no disinfectant was placed, 10 cc. sterile water are added and 1 cc. is transferred to a bottle containing 99 cc. sterile water. These bottles are well shaken, and duplicate Petri dishes are poured from each one, 1 cc. solution being first added to the dish followed by enough nutrient agar to make a satisfactory culture plate. When the dishes set they are inverted and allowed to incubate at  $37.5^{\circ}$  C. for 48 hours. At the end of this time the plates are counted and the ratio of the number of surviving bacteria to the number of colonies on the non-disinfected plate is determined. When plotted against the dilution two curves are obtained, types of which are shown on the accompanying plate. If a number of disinfectants are examined at the same time, it is of course not necessary to repeat the phenol series and the bacteria blank with each. The coefficient of total killing for Disinfectant A is seen to be 2.88, while for B it is 4.76.

A study of a large number of these plates shows that the curves for the so-called emulsion disinfectants are almost straight lines; at most there is but a slight curvature. Thus a small number of points will locate a line with a fair degree of accuracy and the necessity of using small increments of dilution as obtains in the older method is not here present. As is clearly shown in this plot, though desirable, it is not necessary, as in the other methods, that the most concentrated solution of the disinfectant used should produce a sterile tube or plate, that is, show total killing. If at least three points have been found to lie fairly well upon a smooth curve, the line may safely be interpolated until it cuts the axis representing complete killing and the coefficient calculated from this intersection. The results obtained may be duplicated with sufficient precision to warrant confidence in them. This is true not only of a single operation carrying on duplicate determinations, but by two analysts working separately.

	I	II
1.....	4.82	4.58
2.....	5.17	5.05
3.....	6.95	6.64
4.....	9.64	9.30
5.....	4.28	4.08
6.....	2.04	2.24

The above duplicate results obtained by the same analyst will give an idea of the degree of accuracy which may be readily attained.

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## THE LEAD CONTENTS IN SUBLIMED WHITE LEAD—A CALCULATION

By JOHN A. SCHAEFFER  
Received December 11, 1913

The composition of sublimed white lead, the basic sulfate of lead, has become a most important factor to

users of this pigment. Both among rubber manufacturers and producers of paints, it is being found essential that the contents of lead oxide and lead sulfate be known, so that advantage may be fully taken of its characteristic properties. This control necessitates an analysis of the compound in the laboratory.

In analyzing sublimed white lead by the usual method, it is found that the percentage composition can be determined only by an analysis entailing lengthy manipulation, in which the content of lead oxide is directly dependent upon the accuracy of the other determinations, owing to the necessity of estimating its percentage by a calculation based upon the percentage of the other constituents present. The steps in the procedure must therefore be closely watched for slight inaccuracies at all times.

As is well known, the average composition of sublimed white lead is given as follows:

Lead sulfate.....	78.5
Lead oxide.....	16.0
Zinc oxide.....	5.5

That its composition varies only slightly from the above analysis during a long period of time, is shown by its comparison with an average of the entire output of the Picher Lead Company extending over five months time, an average embracing 270 total analyses.

This average shows the composition to be:

Lead sulfate.....	76.68
Lead oxide.....	17.23
Zinc oxide.....	5.79
	99.70

A slightly higher lead oxide and zinc oxide content and a correspondingly lower lead sulfate content is found, than in the usually stated formula. It shows, however, only slight variation. The average total percentage, consisting of lead sulfate, lead oxide, and zinc oxide, was found to be 99.70 per cent. The remaining 0.3 of a per cent is only rarely determined, and when actually sought is found to consist of moisture, occluded gas and ash. A definite ratio exists between the total lead content and the lead sulfate and lead oxide contents, and advantage may be taken of this relation for a rapid and accurate determination of the lead constituents in sublimed white lead.

In order to arrive at the short method for the analysis which is based upon a direct calculation of the lead and zinc contents, it is necessary that the usual method of analysis be considered.

## USUAL METHOD ADOPTED FOR THE ANALYSIS OF SUBLIMED WHITE LEAD

DETERMINATION OF TOTAL SULFATE—Mix 0.5 gram of the sample with 3 grams of sodium carbonate in a beaker. Treat the mixture with 30 cc. of water and boil gently for ten minutes. Allow to stand for four hours. Dilute the contents of the beaker with hot

water; filter off the residue and wash until the filtrate is about 200 cc. in volume. Reject the residue. By this reaction all the lead sulfate is changed to carbonate, the sulfate being transposed into sodium sulfate, which is found in the filtrate.

Acidulate the filtrate with hydrochloric acid and add an excess of about 2 cc. of the acid. Boil, and add a slight excess of barium chloride solution (12 cc. of an 8 per cent solution). When the precipitate has well settled, filter on an ashless filter, wash, ignite and weigh as  $\text{BaSO}_4$ . Calculate the  $\text{BaSO}_4$  to  $\text{PbSO}_4$  by using the factor 2.6 when a half gram is used.

Weight of  $\text{BaSO}_4 \times 1.3 = \text{weight PbSO}_4$ .

On 0.5 gram sample the factor  $\text{BaSO}_4$  to  $\text{PbSO}_4 = 2.6$ .

**DETERMINATION OF LEAD. MOLYBDATE METHOD<sup>1</sup>**—Dissolve 1 gram of the sample in 100 cc. of an acid ammonia acetate solution made up as follows:

Eighty per cent acetic acid . . .	125 cc.
Concentrated ammonia hydroxide . . . . .	95 cc.
Water . . . . .	100 cc.

Add this solution hot and dilute with about 50 cc. of water. Boil until dissolved. Dilute to 200 cc. and titrate in the usual manner with standard ammonium molybdate solution, spotting out on a freshly prepared solution of tannic acid.

Ammonium molybdate is a slightly variable salt, but a solution containing 8.67 grams per liter usually gives a standard solution:

1 cc. = 0.01 gram Pb

Standardize against pure  $\text{PbO}$ , pure  $\text{PbSO}_4$  or clean lead foil.

Deduct the lead found as lead sulfate from the total lead and calculate the residual lead to  $\text{PbO}$ .

**DETERMINATION OF ZINC. FERROCYANIDE METHOD<sup>2</sup>**—Boil 1 gram of the sample in a beaker with the following solution:

Water . . . . .	30 cc.
Ammonium chloride . . . . .	4 grams
Concentrated hydrochloric acid . . . . .	6 cc.

If the sample is not quite dissolved the result is not affected, as the residue is lead sulfate or precipitated lead chloride.

Dilute to 200 cc. with hot water, add 2 cc. of a saturated sodium hyposulfite solution and titrate with a standard solution of potassium ferrocyanide, spotting out on a 5 per cent solution of uranium nitrate. Calculate the zinc to zinc oxide.

**SULFUR DIOXIDE**—Digest 2 grams of the sample with frequent stirring in 5 per cent sulfuric acid for ten minutes in the cold. Add starch indicator and titrate with  $N/100$  iodine solution.

A more accurate method is to add an excess of standard iodine solution to the sample before the addition of the acid and then to titrate the excess of iodine with  $N/100$  sodium thiosulfate solution.

It will be seen from the above method of analysis that the concordance of results depends upon several

<sup>1</sup> Modification of Low's method. "Technical Methods of Ore Analysis," Low, p. 149.

<sup>2</sup> "Technical Methods of Ore Analysis," Low, p. 284.

important factors; namely, the accurate estimation of the total lead content, the zinc content and the complete transposition of the lead sulfate present to lead carbonate with the attendant formation of sodium sulfate from which the sulfate is determined as barium sulfate. The percentage of lead oxide depends wholly upon the accuracy of these determinations, as it is never directly determined.

The following method for ascertaining the lead sulfate and lead oxide contents is based upon a calculation depending upon the percentage of total lead found. The complete analysis can be easily carried out in a half hour.

The essential requisites are the volumetric determination of the zinc present with its subsequent calculation to zinc oxide, and the volumetric determination of the total lead, regardless of the proportion of lead sulfate and lead oxide present. These volumetric determinations are carried out according to the method above outlined.

Using the percentages of zinc oxide and total lead, together with the average total, 99.70 per cent, determined from the large number of analyses, the contents of lead oxide and lead sulfate are readily estimated by the following calculation:

Total percentage of lead compounds present	
= total percentage found of $\text{ZnO}$ , $\text{PbO}$ and $\text{PbSO}_4$ — percentage of $\text{ZnO}$ .	
Total percentage of lead compounds present	
= 99.70 per cent (average total) — percentage $\text{ZnO}$ .	
Atomic weight lead . . . . .	207.1
Molecular weight lead oxide . . . . .	223.1
Molecular weight lead sulfate . . . . .	303.1

As a hypothetical case, we can assume the presence of a 4.70 per cent  $\text{ZnO}$  and 69.00 per cent metallic lead.

Determining the percentage of lead oxide and lead sulfate present by the above formulas we find:

$$\frac{\left( \frac{303.1}{207.1} \times 69.00 \right) - 95.00}{303.1 - 223.1} = \text{per cent PbO} = 16.68$$

$$\frac{\left( \frac{223.1}{207.1} \times 69.00 \right) - 95.00}{223.1 - 303.1} = \text{per cent PbSO}_4 = 78.32$$

$$\frac{\left( \frac{\text{Mol. wt. PbSO}_4}{\text{At. wt. Pb}} \times \% \text{ Pb found} \right) - \% \text{ Pb constituents}}{\text{Mol. wt. PbSO}_4 - \text{mol. wt. PbO}} = \% \text{ PbO present}$$

$$\frac{\left( \frac{\text{Mol. wt. PbO}}{\text{At. wt. Pb}} \times \% \text{ Pb found} \right) - \% \text{ Pb constituents}}{\text{Mol. wt. PbO} - \text{Mol. wt. PbSO}_4} = \% \text{ PbSO}_4 \text{ present}$$

A comparison of the actual results obtained by the complete analysis of sublimed white lead and its calculated composition shows that the values obtained are concordant. Indeed the only essential factors for the short method are accurate determinations of the lead and zinc contents. The removal of several steps in the analysis leads to greater accuracy coupled with a considerable curtailment of time.

A table of comparisons shows the following concordance of results:



No.	Analysis	Lead sulfate	Lead oxide	Zinc oxide	Total lead	Total
1	Complete.....	79.20	15.28	5.23	68.30	99.72
	Calculated.....	79.17	15.30			
2	Complete.....	77.74	16.81	5.11	68.70	99.66
	Calculated.....	77.97	16.62			
3	Complete.....	77.09	16.95	5.73	68.40	99.77
	Calculated.....	76.88	17.12			
4	Complete.....	80.20	14.66	4.86	68.40	99.72
	Calculated.....	80.15	14.69			
5	Complete.....	78.00	16.60	5.11	68.70	99.71
	Calculated.....	77.97	16.62			
6	Complete.....	77.84	17.10	4.86	69.00	99.80
	Calculated.....	77.69	17.15			
7	Complete.....	77.22	16.20	6.23	67.80	99.63
	Calculated.....	77.41	16.06			
8	Complete.....	74.10	20.21	5.48	69.40	99.79
	Calculated.....	74.00	20.22			
9	Complete.....	77.63	15.92	6.23	67.80	99.78
	Calculated.....	77.41	16.06			
10	Complete.....	76.05	17.93	5.73	68.60	99.71
	Calculated.....	76.04	17.93			
11	Complete.....	76.98	17.78	4.98	69.10	99.74
	Calculated.....	76.85	17.87			

That this method will prove of value will be readily appreciated by all chemists who have to determine the percentage composition of any basic sulfate of lead, either for the purpose of meeting specifications or for accurate control of finished products.

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### THE CONSTITUTION OF WHITE LEAD

By EDWIN EUSTON

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The usual view is that the widely used Dutch, or tan-bark stack, process of corrosion of metallic lead to form white lead results in a product containing principally a fixed and definite compound,  $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ . This view is based on the physical appearance of the crust formed under the best conditions, and assumes that the higher percentage of combined carbon dioxide almost always found on analysis is due to admixed normal lead carbonate, and that the lower percentage of carbon dioxide occasionally found results from admixed lead hydroxide. It is certain that a considerable percentage of normal lead carbonate in the crystalline form ("sandy lead") is usually present in the product of the stack process, even to the extent of 5 per cent or more; and under abnormal conditions of corrosion de-hydrated lead hydroxide is found to be present in quantity sufficient even to injure the color of the white lead. The possibility, or even the probability, therefore, of either or both normal lead carbonate and some form of lead hydroxide being present in stack process white lead must be admitted. The purpose of the writer is to consider whether true white lead (the so-called basic carbonate of lead) consists substantially of a fixed and definite compound,  $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ , admixed with chance amounts of normal lead carbonate and lead hydroxide, or whether some other form or forms of combination of the elements involved may not better accord with the facts.

During the long time required in the stack process to effect the commercial degree of corrosion, usually 100 to 120 days, no important control can be exercised over the process, and even in the separate tiers of the same stack, wide variations of the governing conditions

of heat, ventilation, moisture and vaporization of the acetic acid occur, rendering the stack process entirely unsuitable as a means of investigating experimentally the steps in the formation of white lead and the nature of the product. Precipitation by carbon dioxide gas from basic lead acetate solution, as first suggested by Thenard as a means of forming white lead, has been found to be subject to so many difficulties of control that heretofore no results of value have been derived from this method. Yet when due care is exercised to ensure uniformity of treatment of the entire mass of solution and precipitate, when the apparatus used is of sufficient size (say, 1000 pounds product per hour), and when proper tests are known, close control of the precipitation process is attainable; and in many thousand repetitions on this manufacturing scale the writer has found that very definite results may be obtained, throwing new light on the series of changes occurring when basic lead acetate solution is subjected to the action of carbon dioxide.

For practical reasons an approximately di-basic solution of lead acetate formed from about 4 per cent acetic acid is preferable, uniformly circulated (without permitting separation of the resulting precipitate from the liquid) by spraying a number of times through an atmosphere of moderately or strongly concentrated carbon dioxide gas, at room temperature. When the precipitation is slowly performed under standard conditions, the precipitate first appearing is colloidal in character and analyses 8.6 per cent  $\text{CO}_2$  or slightly higher, corresponding to the formula  $\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ . When more quickly performed, the precipitate contains 9.0 to 10.0 per cent  $\text{CO}_2$ , therefore also less than the 11.3 per cent  $\text{CO}_2$  corresponding to the formula  $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$  constituting the usually accepted view of the principal compound in white lead. On continuing the treatment, the percentage of combined  $\text{CO}_2$  increases gradually until it approximates 16.6 per cent, corresponding to the formula of the normal carbonate  $\text{PbCO}_3$ , after which no further precipitation and no further change in the composition of the already formed precipitate occurs. Throughout this treatment the increase in the  $\text{CO}_2$  percentage in the precipitate is progressive and gradual, with no evidence of the formation of hypothetical intermediate compounds such as the supposed  $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ , or such as  $3\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ . The change in the solution as the available lead is precipitated is gradual, from strong alkalinity to slight acidity. Similarly, the properties of the precipitate indicate only gradual change as the process progresses, except that when the solution passes the point of exact neutrality the "apparent density" of the precipitate suddenly and sharply increases, but thereafter resumes the more gradual rate of increase which is also characteristic in the earlier stage of the precipitation. This sudden increase in "apparent density" is doubtless due to coagulation occurring when the solution becomes acid. Analyses do not indicate any fixed and definite composition of the precipitate when this sudden increase in "apparent density" occurs, as the determinations may range variously from 11.0 per cent to even 13.5

per cent  $\text{CO}_2$ . The foregoing, therefore, affords no evidence of the formation of the usually assumed compound  $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ , but on the contrary shows the initial formation of a precipitate of the composition  $\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$  and the gradual change to the normal carbonate.

Lead hydroxide is soluble in a solution of cane sugar in water. At no stage in the above described process is the separated and washed precipitate appreciably soluble in cane-sugar solution. Therefore, the precipitates described are not simple mixtures of normal carbonate and of lead hydroxide, but hold the lead hydroxide in some form of combination with all or part of the carbonate. This fact, in connection with the analyses of the first formed precipitate, shows that the first product obtained is a basic carbonate of the formula  $\text{PbCO}_3 \cdot (\text{OH})_2$ . Inasmuch as the final product obtained by continuing the process to the extreme degree is  $\text{PbCO}_3$ , the question then becomes whether these two compounds,  $\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$  and  $\text{PbCO}_3$ , when mixed in various proportions, constitute white lead, or whether other compounds must also be postulated.

As mixtures of  $\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$  and  $\text{PbCO}_3$  in proper proportions give all the intermediate percentages of combined carbon dioxide between 8.6 per cent and 16.6 per cent, no other compounds than these two need to be assumed from the point of view of composition. A mixture of one equivalent of  $\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$  with one equivalent of  $\text{PbCO}_3$  will give the average 11.3 per cent  $\text{CO}_2$  of the heretofore assumed  $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ , and the physical properties of a sample of white lead analyzing 11.3 per cent  $\text{CO}_2$  and directly prepared are identical with the physical properties of a sample of the same average composition obtained by mechanically mixing together separately prepared equivalent quantities of  $\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$  and of  $\text{PbCO}_3$ , *e. g.*, the space occupied by 20 grams of the pulverized sample settling freely under water in a 200 cc. cylinder, the amount of linseed oil necessary to form a paste, the ease of miscibility with linseed oil, also the opacity and spreading power when mixed as a paint. This same result is true for all other variations of composition between 8.6 per cent and 16.6 per cent  $\text{CO}_2$ , *i. e.*, the entire range.

The molecular volume affords further evidence that no other compounds than  $\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$  and  $\text{PbCO}_3$  are present in white lead properly prepared:

	Molecular volume	Ratio	Percentage linseed oil required to form paste	Ratio
(a) $\text{PbCO}_3$ .....	57.0	1.0	7 (actual)	1.0
(b) $\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ .....	97.8	1.71	12 (actual)	1.7
(c) $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ .....	154.8	2.71	19 (indicated)	2.7
(d) $3\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ .....	211.8	3.71	26 (indicated)	3.7

The close correspondence between the ratios for calculated molecular volume and for actual oil requirement in the case of (a) and (b) is very striking. The indicated oil requirements for the hypothetical compounds (c) and (d), *viz.*, 19 per cent and 26 per cent, are entirely too high to accord with the known oil requirements of white lead of the corresponding

analyses, and would imply that as the percentage of carbon dioxide in white lead increases, the oil requirement would rapidly increase until, when the normal carbonate should be reached, a sudden great drop in oil requirement would result. Certainly this is not the case, for actually the oil requirement, as the percentage of carbon dioxide increases, shows gradual reduction from 12 per cent to 7 per cent for all intermediate stages. Instead of the indicated oil requirement of 19 per cent for (c), therefore, this figure becomes

$$(7 \times 260.5) + (12 \times 507) = 10.27 \text{ per cent,} \\ 773.5$$

which accords with the facts, provided allowance is made for gain in compactness due to the intermeshing of two sizes of particles, resulting in an actual requirement of about 9 per cent oil.

Inasmuch as the Dutch or stack process also involves the use of basic lead acetate solution and carbon dioxide gas, there is no reason to consider that the course of reactions in the stack process (in which the reactions cannot be watched) differs from the now known course of reactions in the precipitation process (in which the reactions can be watched); and, except in its comparative coarseness and granularity and its less degree of whiteness due to tan-bark and other stains, stack process lead has no characteristics different from those of a precipitated white lead known to contain the two compounds  $\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$  and  $\text{PbCO}_3$ . The conclusion is clear, therefore, that white lead does not contain a compound of the heretofore assumed formula  $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ , but that on the contrary white lead consists of a mixture of the two amorphous compounds  $\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$  and  $\text{PbCO}_3$ , complicated in the case of stack white lead by the presence of some lead carbonate in crystalline form and occasionally some form of lead hydroxide due to abnormal conditions in the corroding stack.

EUSTON WHITE LEAD CO.  
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## ON THE DETERMINATION OF TITANIUM AS PHOSPHATE

By GEORGE S. JAMIESON AND RICHARD WRENSHALL

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Several years ago Eric John Ericson<sup>1</sup> described a method for the determination of titanium in ferrotitanium and in ores. The method was based upon the precipitation of titanium phosphate in acid solution by the addition of ammonium phosphate and boiling, after reducing the iron to the ferrous state by means of ammonium bisulfite or sulfur dioxide. He gave the factor 0.336 for calculating the titanium from the weight of the phosphate, assuming that the latter has the formula  $\text{Ti}_2\text{P}_2\text{O}_8$ .

On account of the simplicity and rapidity of this method its accuracy and application have been studied in this laboratory. Some modifications of the original method have been found desirable and its application to the separation of titanic acid from alumina has been worked out. A series of eighteen experiments

<sup>1</sup> *Iron Age*, Aug. 27, 1903, p. 4.

was made with standard solutions of ferric and titanous sulfates containing enough sulfuric acid to keep the salts in solution, but the quantities of free sulfuric acid present were not determined.

The standard titanium solutions employed in this research were prepared from pure potassium titanium fluoride with the exception of one solution made from a titanium oxalate of excellent quality. The titanium salts were converted into the sulfate by repeated evaporation with sulfuric acid in platinum dishes. The solutions were standardized by precipitating the titanium with ammonia from measured volumes, finally weighing the dioxide and calculating the strength of the solution in terms of titanium. The values obtained were checked by precipitating the titanium by the sodium thiosulfate method and weighing the dioxide.

In each case 15 cc. of 1 : 1 hydrochloric acid were added to measured volumes of these solutions, water was added to make the volume 100 cc., sulfur dioxide was passed through for 10 minutes, the liquid was heated to boiling and 20 cc. of a 10 per cent solution of ammonium phosphate were added. The boiling was continued for a half hour; the precipitate was allowed to settle for an hour or more; it was then filtered and washed with hot water on a Gooch crucible in which it was finally ignited for 15 minutes at the highest temperature of the Bunsen burner and weighed. The method of Ericson was closely followed here except that the Gooch crucible was used instead of paper for filtering, on account of the tendency of the precipitate to run through a paper filter. In order to make satisfactory use of the Gooch crucible, it is necessary to use moderate suction and to avoid allowing all the liquid to pass out of the crucible until thorough washing has been effected, for it is impossible to wash the precipitate after it has become compact and has cracked. Except with very small quantities of titanium, the results obtained were satisfactory. Low results were obtained when less than 0.007 gram of titanium was present, which appear to be due to the failure of the precipitate to collect in a filterable form. It probably remains in a colloidal condition. The writers have found that with such small quantities of titanium less acid must be used and after precipitation and boiling, it is advisable to let the liquid stand for at least 6 hours, then to warm on the steam bath and filter. With this treatment the loss appears to be no greater with about 0.002 gram of titanium than with larger quantities.

When an attempt was made to apply Ericson's method to some ores containing 0.5 to 8 per cent of titanium it was found that no precipitate or only a small one was obtained if the ores had been dissolved by treatment with hydrochloric and sulfuric acid and evaporation with a rather large amount of sulfuric acid instead of being dissolved by a potassium bisulfate fusion. This was evidently due to the presence of the large amount of sulfuric acid in addition to the hydrochloric acid used. Therefore, when this convenient method for dissolving titanium ores is employed, it is necessary to neutralize the sulfuric acid,

best with ammonia, before proceeding with the determination. Titanium ores or minerals not decomposed by the acid treatment just described, are rendered soluble by fusion with potassium bisulfate in the usual manner.

In the analyses in the table given below, the sulfuric acid present in each solution was neutralized with ammonia before adding the hydrochloric acid; the precipitates were allowed to settle at least six hours, then the solutions were heated on the steam bath for about 20 minutes before filtering.

No.	Fe taken	Ti taken	Ti found	Error	Cc. 1 : 1 HCl used
1.....	0.000	0.0019	0.0018	-0.0001	1
2.....	0.000	0.0030	0.0027	-0.0003	3
3.....	0.000	0.0030	0.0034	+0.0004	3
4.....	0.043	0.0010	0.0010	+0.0000	2
5.....	0.086	0.0010	0.0009	-0.0001	3
6.....	0.086	0.0030	0.0029	-0.0001	3
7.....	0.086	0.0010	0.0009	-0.0001	3
8.....	0.086	0.0019	0.0011	-0.0008	6
9.....	0.086	0.0010	0.0002	-0.0008	6
10.....	0.086	0.0039	0.0032	-0.0007	10
11.....	0.043	0.0100	0.0101	+0.0001	5
12.....	0.043	0.0154	0.0152	-0.0002	5
13.....	0.043	0.0154	0.0151	-0.0003	5
14.....	0.100	0.0248	0.0245	-0.0003	15
15.....	0.100	0.0248	0.0244	-0.0004	15
16.....	0.100	0.0260	0.0256	-0.0004	15
17.....	0.110	0.0260	0.0258	-0.0002	15

In these experiments a volume of about 50 cc. was used instead of 100 cc., as in the case of the first series of experiments. It will be observed that in the first 10 experiments very small amounts of titanium were taken in order to determine the conditions under which they could be satisfactorily precipitated and filtered. It is evident from these experiments that when 1-3 mg. of titanium are present, it is necessary to keep the amount of free 1 : 1 hydrochloric acid down to about 3 cc. in 50 cc. solutions, otherwise low results will be obtained.

Experiments were made to find if titanium phosphate could be precipitated in the presence of tartaric acid and it was found that this could be done quantitatively although in a recent article Thornton<sup>1</sup> states that titanium cannot be precipitated by any reagent in the presence of tartaric acid. To the solutions containing measured quantities of titanium and ferric sulfates, about 2 grams of tartaric acid were added and enough ammonia to make them slightly alkaline. Then hydrogen sulfide was passed into the warm solutions until the iron was reduced and precipitated as sulfide. The solutions were treated with 10-15 cc. of 1 : 1 hydrochloric acid, depending upon the amount of iron present, and heated until the iron sulfide was dissolved. Then 20 cc. of the 10 per cent ammonium phosphate reagent were added and the experiments from this point were identical with those described above. In the first four experiments the ferrous sulfide was filtered off and washed with hot water containing a little ammonium sulfide, while in the last four the ferrous sulfide was not filtered, but dissolved as previously directed. No advantage was gained by removing the iron from the solution. The following results were obtained.

<sup>1</sup> *Am. J. Sci.*, **34**, 214.



No.	Fe taken	Ti taken	Ti found	Error
1.....	0.086	0.0207	0.0206	-0.0001
2.....	0.043	0.0050	0.0049	-0.0001
3.....	0.043	0.0030	0.0024	-0.0006
4.....	0.043	0.0040	0.0039	-0.0001
5.....	0.043	0.0060	0.0059	-0.0001
6.....	0.200	0.0249	0.0253	+0.0004
7.....	0.100	0.0186	0.0186	±0.0000
8.....	0.100	0.0249	0.0248	-0.0001

The choice of methods for the reduction of the iron is largely a matter of personal preference, since both give equally good results as seen in the tables of test analyses given above. However it may be said that the reduction of the iron in our ammoniacal solution is somewhat quicker than that by sulfur dioxide in a hydrochloric acid solution.

In applying this method to the determination of titanium in some ores, which were previously found to be completely decomposed by acid treatment, the procedure was as follows: To 0.5 gram of very finely pulverized sample, 25 cc. of concentrated hydrochloric acid were added and the solution was heated upon the steam bath until no further action was observed. About 20 cc. of 1 : 2 sulfuric acid were added and the solution was cautiously evaporated to sulfuric acid fumes and then heated for an hour at a temperature just below the boiling point. After cooling, 30 cc. of water were added and the solution was warmed until the soluble salts had dissolved. The insoluble matter was filtered, washed three times with very dilute sulfuric acid, and finally with water at room temperature. The insoluble matter was tested and was found to be free from titanium. The filtrate was diluted to exactly 500 cc., mixed thoroughly, and aliquot parts were taken so that the ignited precipitate would not weigh over 90 mg., as it was not practical to attempt the filtration of larger amounts of this gelatinous precipitate. To each aliquot part 2 grams of tartaric acid were added and the method from this point was identical with that described above. Three titanic iron ores were analyzed with the following results.

Ore	Ti found	Ti by the volumetric method <sup>1</sup>
A.....	13.00%	13.18%
A.....	13.17	...
A.....	13.20	...
B.....	24.19	...
B.....	23.99	24.22
B.....	24.22	...
C.....	15.82	...
C.....	15.86	15.94
C.....	16.01	...

It is recommended that for the general application of this method to the determination of titanium in the presence of relatively large amounts of iron, the titanium be precipitated from a solution of about 100 cc. volume which contains 15 cc. of 1 : 1 hydrochloric acid. Furthermore, it is recommended that enough substance be taken so that at least 10 mg. of titanium shall be present in the solution.

It was found that titanium could be separated from aluminium and determined in the same manner as when iron is present, but that it was necessary to use

more hydrochloric acid in order to prevent the precipitation of aluminium phosphate. The method employed was to add 1-2 grams of tartaric acid to the solution of titanium and aluminium sulfates and enough ammonia to make it slightly alkaline. (The tartaric acid was used to prevent the formation of the hydroxide.) Then a measured quantity of hydrochloric acid was added and the analysis was completed in the same way as when iron was present. A volume of about 100 cc. was used in the following experiments:

No.	AlO taken	Ti taken	Ti found	Error	Cc. conc. HCl used
1.....	0.063	0.0273	0.0277	+0.0004	10
2.....	0.060	0.0310	0.0308	-0.0002	12
3.....	0.070	0.0248	0.0245	-0.0003	10
4.....	0.063	0.0248	0.0249	+0.0001	9
5.....	0.110	0.0210	0.0214	+0.0004	10
6.....	0.100	0.0260	0.0263	+0.0003	11
7.....	0.120	0.0310	0.0309	-0.0001	14
8.....	0.060	0.0223	0.0224	+0.0001	15
9.....	0.060	0.0186	0.0189	+0.0003	8
10.....	0.050	0.0186	0.0182	-0.0004	15
11.....	0.070	0.0248	0.0245	-0.0003	10
12.....	0.060	0.0122	0.0119	-0.0003	7
13.....	0.050	0.0248	0.0292	+0.0044	5
14.....	0.100	0.0310	0.0473	+0.0163	5
15.....	0.150	0.0186	0.0233	+0.0047	7
16.....	0.100	0.0248	0.0288	+0.0040	5
17.....	0.070	0.0310	0.0351	+0.0041	7

These experiments indicate that with a volume of 100 cc. containing 0.05-0.15 gram alumina it is necessary to have an excess of at least 8 cc. of concentrated hydrochloric acid in order to get a satisfactory separation of the titanium.

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### THE DETERMINATION OF PHENOL IN THE PRESENCE OF HEXAMETHYLENETETRAMINE AND FORMALDEHYDE

By L. V. REDMAN, A. J. WEITH AND F. P. BROCK

Received December 2, 1913

During a research into the rate of condensation between phenols and active methylene groups in the production of synthetic resins it became necessary for us to find a rapid and accurate method for the determination of phenols in the presence of substances containing methylene groups, *e. g.*, formaldehyde, hexamethylenetetramine, etc.

In previous papers<sup>1</sup> we have described a bromination method which serves for the very accurate and rapid quantitative determination of phenol in a water solution. The method consisted in diluting the phenol to *N*/1000, in acid solution, shaking the solution for 1 minute after the bromide-bromate solution is added, then adding KI, shaking again for 1 minute and titrating the excess iodine with thiosulfate. The whole operation was carried out at 20-25° C.

The present paper deals with the determination of phenol in a water solution in the presence of hexamethylenetetramine or formaldehyde or both, using the above method with whatever modifications are mentioned later in this paper.

<sup>1</sup> A modification of the method in Gooch's "Methods in Chemical Analysis," page 242.

<sup>1</sup> Redman and Rhodes, *This Journal*, **4** (1912), 655; Redman, Weith and Brock, *Ibid.*, **5** (1913), 389.

The first of these probable interfering substances to be tried was hexamethylenetetramine and the results are given in the accompanying table. Hexamethylenetetramine does not interfere in the determination of phenol by bromine when present up to 1 per cent of the total solution,<sup>1</sup> *i. e.*, 30 mols. of hexamethylenetetramine to 1 mol. of phenol. Much larger amounts than this have been tried. As much hexamethylenetetramine as 15 per cent of the total solution, *i. e.*, 450 mols. of hexamethylenetetramine to 1 mol. of phenol, has been added in a single determination of the phenol without changing the results. The only intermediate change noted when the hexamethylenetetramine was present in large quantities was a tendency on the part of the free iodine to form a brick-red granular precipitate, or a beautiful iridescent crystalline precipitate with the excess hexamethylenetetramine. This precipitate which is either the tetra-iodo-hexamethyltetramine or di-iodo-hexamethyltetramine dissolves up readily on the addition of the thiosulfate giving back the free iodine, and does not in any way interfere in the quantitative determination.

The presence of free formaldehyde, however, interferes very seriously with the phenol determination. Results that are 7-8 per cent too high are obtained when the total solution is one per cent formaldehyde as is shown in the table (Expts. 5 and 6). The higher the percentage of formaldehyde present the higher the results which are obtained for the phenol present in the solution until, for 40 per cent formaldehyde, bromine is absorbed in very large quantities and no precipitation of tribromophenol takes place, and the determination of phenol by this method is quite impossible.

It is evident then that if hexamethylenetetramine does not interfere with the determination, and formaldehyde does interfere, the addition of ammonia to the solution in which formaldehyde is present as an interfering substance may, by forming hexamethylenetetramine with the aldehyde obviate the trouble.

The addition of ammonia to a phenol solution containing formaldehyde was tried and the results are given in the table, Expts. 7, 8, 9, 10. If the unknown phenol solution be made 2 *N* with ammonia and the whole allowed to stand for 5 minutes, the formaldehyde is transformed over into hexamethylenetetramine or some intermediate non-interfering compound and the determination of the phenol may be made with speed and accuracy. Allowing the ammonia, formaldehyde and phenol to remain together in the water solution longer than 5 min., *e. g.*, 18 hours, before the determination is made does not affect the results as is shown in Expts. 9 and 10.

This method of determining phenol in the presence of formaldehyde would not hold if a condensing agent had been present previously or if the solution had been treated in a way which tended to form oxybenzylalcohol, saligeno-saligenin, etc.

In determining phenol in the presence of hexamethylenetetramine the bleaching of the starch iodide

<sup>1</sup> The total solution refers to the volume after the dilution has been made with the water and acid, before adding the bromine solution.

No.	Amount of interfering substance	Cc. of NH <sub>3</sub> added	Time after ammonia was added, to dech.	Cc. % of HCl added	Cc. % of sol. used	Thiosulfate sol. used	Per cent of phenol determined
1		0			16.92	3.42	100
2		0			17.10	3.59	100
3	1 gram hexa	0			16.97	3.56	99.36
4	1 gram hexa	0			18.68	5.17	100.19
5	3 cc. 40% CH <sub>2</sub> O	0			17.00	2.52	106.92
6	3 cc. 40% CH <sub>2</sub> O	0			18.46	3.70	108.32
7	3 cc. 40% CH <sub>2</sub> O	10	5 min	17	16.40	2.92	99.72
8	3 cc. 40% CH <sub>2</sub> O	10	5 min	17	15.89	2.40	99.30
9	3 cc. 40% CH <sub>2</sub> O	10	18 hrs.	17	16.98	3.54	99.50
10	3 cc. 40% CH <sub>2</sub> O	10	18 hrs.	17	16.62	3.16	99.51

Water of dilution = 100 cc.

Phenol solution used = 15 cc.

Bromide-bromate sol. = 0.09970 *N*.

Hydrochloric acid = 37% solution.

*N*/10 ammonia = 28% solution.

Thiosulfate = 0.09825 *N*.

color by the thiosulfate is slightly retarded by the presence of hexamethylenetetramine and it is necessary to give a few seconds after the addition of the thiosulfate to allow the blue color time to disappear.

### CONCLUSIONS

I. Phenol in the presence of hexamethylenetetramine may be determined by the method already described for the determination of phenol.

II. Formaldehyde interferes with the volumetric determination of phenol by bromine.

III. The addition of strong ammonia to the phenol-formaldehyde solution forms with the aldehyde, hexamethylenetetramine or some intermediate ammonia-aldehyde product which does not interfere with the quantitative determination of phenol.

DEPARTMENT OF INDUSTRIAL RESEARCH  
UNIVERSITY OF KANSAS, LAWRENCE

### ULTIMATE ANALYSES OF COAL TAR PITCHES

By C. R. DOWNS

Received December 6, 1913

In connection with an investigation of coal tar pitches, the ultimate analyses of some briquet pitches were obtained.

#### ANALYSES OF THREE TYPICAL COAL TAR BRIQUET PITCHES OF AMERICAN ORIGIN

	Pitch No. 1 Per cent	Pitch No. 2 Per cent	Pitch No. 3 Per cent
Carbon.....	92.05	92.37	93.09
Hydrogen.....	4.83	4.96	5.01
Nitrogen.....	0.95	0.61	0.89
Sulfur.....	0.92	1.00	0.85
Mineral ash.....	0.09	0.78	0.35
Oxygen (by difference).....	1.16	0.28	0.90
Free carbon.....	33.7	31.3	26.4

Melting point 112° C., 87° C., 84° C.

The carbon and hydrogen were determined by the regular combustion method, taking proper precautions to eliminate the sulfur and nitrogen. The sulfur was determined by combustion in a bomb with oxygen under pressure (sodium peroxide being used to insure complete oxidation), and precipitated as barium sulfate. The Kjeldahl method was used for the nitrogen.

The melting points and free carbon contents of the pitches were also determined in the usual way.

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## NOTE ON THE DETECTION OF NICKEL IN FATS

By ROBERT H. KERR

Received November 22, 1913

In testing samples of cottonseed oil, hydrogenated cottonseed oil, and mixtures of fats containing cottonseed oil, for nickel by the method of Boemer<sup>1</sup> a fugitive red color sometimes appears after the addition of the dimethylglyoxime and ammonia. This color closely resembles that obtained when a trace of nickel is present, but differs from that of nickel dimethylglyoxime, in that it is fugitive, appearing immediately after the addition of the ammonia, never before, and fading away almost entirely within a few minutes. Its appearance is apt to be very confusing, particularly to one not thoroughly familiar with it.

As there is no known inorganic body capable of giving such a reaction with dimethylglyoxime, it would appear probable that this reaction is due to some organic base contained in the oil and extracted from it by the hot hydrochloric acid. The fact that this reaction has been observed only with cottonseed oil, taken together with the well known fact that cottonseed contains numerous basic organic bodies, appears to corroborate this view. This hypothesis leads naturally to the conclusion that the trouble might best be prevented by the complete destruction of all organic matter contained in the acid extract.

Experiments have upheld this conclusion. A number of samples which had previously been found to show the fugitive red color to a marked degree have been found to show no trace of it after the destruction of all organic matter in the acid extract. As a result of this observation the following modification of the Boemer method is now proposed for the detection of nickel in fats.

Ten grams of the fat to be tested are heated on the steam bath with 10 cc. of hydrochloric acid (specific gravity 1.12), with frequent shaking for 2-3 hours. The fat is then removed by filtering through a wet filter paper, the filtrate being received in a white porcelain dish. The filtrate is evaporated to dryness on the steam bath, 2-3 cc. of concentrated nitric acid being added, after it has been partly evaporated, to insure the destruction of all organic matter. After the evaporation is complete the residue is dissolved in a few cubic centimeters of distilled water and a few drops of a one per cent solution of dimethylglyoxime in alcohol added. A few drops of dilute ammonia are then added. The presence of nickel is shown by the appearance of the red colored nickel dimethylglyoxime. The amount of nickel present may be estimated by comparing the color developed with that developed in a standard solution of a nickel salt.

A considerable number of samples, some of which had previously been found to give the fugitive color mentioned above, have been examined by this method without any instance of the appearance of color not due to nickel. The residues from the evaporation are also purer and more readily soluble than when nitric acid is not used. A larger sample of the fat may

be taken if desired. If this is done the amount of hydrochloric acid used for extraction as well as the amount of nitric acid added to the filtrate should be correspondingly increased. Samples as large as 200 grams have been handled with satisfactory results.

BIOCHEMICAL DIVISION, BUREAU OF ANIMAL INDUSTRY  
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WASHINGTON

## RECENT ANALYSES OF THE SARATOGA MINERAL WATERS. IV

By LESLIE RUSSELL MILFORD

Received December 6, 1913

That the restoration of the mineral waters to the Saratoga basin is being accomplished, is evident by the data which the Reservation Commission has secured since the State undertook its protective policy with regard to the springs. A great amount of information is available concerning the conditions of the springs, the influences which cause them to flow and also those which affect the flow and degree of mineralization of the water. A few years will have to elapse before the springs will have adjusted themselves to all natural conditions which were present before the gas companies began pumping the gas from the wells. Whether or not the former degree of mineralization will ever be reached cannot be stated, but a uniform head, steady flow and fair degree of mineralization has been obtained.

The amount of minerals which these waters held in solution was dependent on the quantity of carbon dioxide which impregnated the water and the pressure exerted at the mineral water vein. For over twenty years, as was stated in a previous paper, an exhaustive pumping of this gas was carried on and a great depletion of the mineral water basin took place, depriving the area of a great amount of energy which nature had furnished for the maintenance of her natural fountains. Since April, 1911, weekly chlorine and alkalinity tests have been made on these waters, by the writer, and these determinations show a fairly constant mineralization varying only with slight physical disturbances. As the main constituents of these waters are the chlorides of sodium, potassium, lithium and ammonium and the bicarbonates of calcium, magnesium, sodium, and barium, these two determinations, chlorine and alkalinity, gave a quick estimation of over 90 per cent of the total mineralization. If either of these should show a change we would have some idea from week to week concerning the condition of the springs.

## DESCRIPTION OF THE SPRINGS

*The Geyser Spring* is situated under the old nut and bolt factory near Geyser pond. It was drilled in 1870 with the intention of securing a supply of fresh water but unexpectedly produced mineral water, the vein having been struck at about 142 feet below the surface of the ground. This spring became very famous and was frequently called the "spouting spring." Its discovery first suggested the idea of boring artesian wells for mineral water and the creation of the carbonic

<sup>1</sup> Chem. Rev. Fett. u. Harz. Ind., Jahr. 19, Heft 9.



acid gas industry. This spring originally had a large flow and would throw a stream 25 feet above the ground. This gradually died out and the spring failed to flow for many years, so special attention was given

a considerable depth with foreign matter. It was therefore reamed to a uniform size, cleaned and explored from top to bottom in order to locate the best mineral water vein. The tubing was completed in

IONS, RADICALS AND OXIDES DETERMINED RESULTS IN MILLIGRAMS PER LITER

Date of analysis	Geyser spring			Washington spring		Old red spring		New red spring	Columbian spring	
	1 —1871	2 Aug 12, 1905	3 July 3, 1912	4 1843	5 Sept. 4, 1912	6 —	7 Aug. 11, 1912	8 July 17, 1912	9 —	10 Apr. 9, 1913
Formula										
SiO <sub>2</sub> .....	12.39	20.80	14.80	25.70	41.25	55.76	51.75	79.40	35.12	47.80
SO <sub>4</sub> .....	3.00	1.40	13.08	0.69	19.96	(a)	5.35	6.39	(a)	40.13
HCO <sub>3</sub> .....	5344.61	4353.20	3540.10	2192.15	1618.84	2116.55	1138.64	1463.22	1818.80	1315.08
NO <sub>3</sub> .....	(a)	Trace	Trace	(a)	0.09	(a)	Trace	Trace	(a)	1.77
NO <sub>2</sub> .....	(a)	None	Trace	(a)	Trace	(a)	Trace	Trace	(a)	Trace
PO <sub>4</sub> .....	Trace	None	None	(a)	None	(a)	None	None	(a)	None
BO <sub>3</sub> .....	Trace	Trace	Trace	(a)	Trace	(a)	Trace	Trace	(a)	Trace
AsO <sub>4</sub> .....	None	None	None	(a)	None	(a)	None	None	(a)	None
Cl.....	6030.43	1025.10	1340.06	1909.64	468.55	923.78	226.24	541.87	2774.28	225.34
Br.....	29.92	11.80	13.64	5.42	2.39	(a)	2.39	8.18	Trace	8.05
I.....	3.59	1.00	0.76	32.54	0.19	(a)	0.46	0.30	37.12	0.07
Fe.....	5.26	(a)	9.46	(a)	36.60	(a)	10.72	12.56	29.96	9.18
Fe and Al.....	(a)	8.40	11.83	20.44	66.46	25.18	24.82	19.99	(a)	10.85
AlO <sub>3</sub> .....	Trace	(a)	4.48	Trace	56.31	Trace	26.58	14.02	(a)	3.14
Mn.....	(a)	(a)	Heavy trace	(a)	None	(a)	Trace	Heavy trace	(a)	None
Ca.....	2913.70	116.40	426.85	357.47	231.93	428.96	130.12	281.95	288.08	217.28
Mg.....	424.42	60.60	116.02	190.98	100.28	120.75	59.96	73.71	132.98	74.17
Ba.....	18.24	2.60	4.12	(a)	1.41	(a)	2.82	2.70	(a)	1.06
Sr.....	3.04	Trace	0.48	(a)	None	Trace	Trace	Trace	(a)	0.10
K.....	222.35	29.00	136.04	2.65	78.20	61.60	32.83	38.88	Trace	47.47
Na.....	4123.56	2010.90	1386.65	1277.15	386.49	634.85	222.68	400.07	1878.39	234.39
Li.....	12.35	3.60	2.76	(a)	0.80	1.66	1.35	1.41	(a)	0.61
NH <sub>4</sub> .....	(a)	11.40	14.62	(a)	2.25	(a)	2.27	3.45	(a)	1.64
Oxygen to form Al <sub>2</sub> O <sub>3</sub> .....	Trace	(a)	2.11	Trace	26.45	{ 10.79 }	12.48	6.59	(a)	1.47
Oxygen to form Fe <sub>2</sub> O <sub>3</sub> .....	...	...	...	...	...	{ ... }	...	...	...	...
F.....	Trace	...	...	...	...	...	...	...	...	...

## HYPOTHETICAL FORM OF COMBINATION

NH <sub>4</sub> Cl.....	(a)	33.80	39.40	(a)	6.68	(a)	6.74	10.23	(a)	5.15
LiCl.....	74.91	21.80	16.75	(a)	5.00	10.07	8.19	8.53	(a)	3.70
KCl.....	395.23	43.90	246.84	(a)	146.89	117.46	60.22	66.66	(a)	82.93
NaCl.....	9528.76	1588.80	1951.08	3148.23	643.05	1416.99	307.12	817.85	4573.71	295.59
KBr.....	43.88	17.50	20.00	8.07	3.50	(a)	3.50	12.00	Trace	12.00
KI.....	4.71	1.30	1.00	(b) 42.65	0.25	(a)	0.60	0.40	(c) 48.55	0.10
Na <sub>2</sub> SO <sub>4</sub> .....	4.44	2.10	19.36	1.02	29.52	(a)	7.91	9.46	(a)	59.34
Na <sub>2</sub> BO <sub>3</sub> .....	Trace	Trace	Trace	(a)	Trace	(a)	Trace	Trace	(a)	Trace
Na <sub>2</sub> NO <sub>3</sub> .....	(a)	Trace	Trace	(a)	0.12	(a)	Trace	Trace	(a)	2.43
Na <sub>2</sub> NO <sub>2</sub> .....	(a)	None	Trace	(a)	Trace	(a)	Trace	Trace	(a)	Trace
Na(HCO <sub>3</sub> ).....	1363.26	5058.30	2238.22	139.62	452.54	282.57	362.63	275.32	288.38	358.76
Ba(HCO <sub>3</sub> ) <sub>2</sub> .....	34.44	4.90	7.78	(a)	2.67	(a)	5.33	5.10	(a)	2.00
Sr(HCO <sub>3</sub> ) <sub>2</sub> .....	7.27	Trace	1.14	(a)	None	Trace	Trace	Trace	(a)	0.23
Mg(HCO <sub>3</sub> ) <sub>2</sub> .....	2553.77	364.90	704.24	1149.15	603.38	726.54	324.70	447.42	800.14	446.29
Ca(HCO <sub>3</sub> ) <sub>2</sub> .....	2913.70	471.40	1728.78	1445.41	937.82	1734.52	768.75	1141.89	1164.84	878.58
Fe(HCO <sub>3</sub> ) <sub>2</sub> .....	16.74	26.70	30.08	65.09	116.56	(a)	34.14	39.94	95.42	29.34
MnO <sub>4</sub> .....	(a)	(a)	Heavy trace	(a)	None	(a)	Trace	Heavy trace	(a)	None
FeO.....	...	...	...	...	...	{ 35.97 }	...	...	(a)	...
AlO.....	Trace	(a)	4.48	Trace	56.31	{ 26.58 }	14.02	...	(a)	3.14
SiO <sub>2</sub> .....	12.39	20.80	14.80	25.70	41.25	55.76	51.75	79.40	35.12	47.80
Total solids in solution (computed).....	16953.50	7656.20	7023.92	6014.83	3045.54	4379.88	1968.16	2928.22	6994.73	2227.28
Residue on evaporation dried at 105° C.....	(a)	(a)	5232.00	(a)	2175.00	(a)	1266.50	2138.00	(a)	1471.00
Temperature.....	7.8° C.	(a)	10.0° C.	7.2° C.	9.5° C.	(a)	11.1° C.	11.6° C.	10° C.	8° C.
Organic matter.....	Trace	...	...	...	...	...	...	...	...	...

(a), not given. (b), equivalent of NaBr reported. (c), equivalent of NaI reported.

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Mineral waters of the U. S. and their therapeutic uses by J. H. Crook, 1899.

The mineral springs of Saratoga, N. Y. State Education Dept. Museum, Bulletin No. 159 by James F. Kemp, 1912.

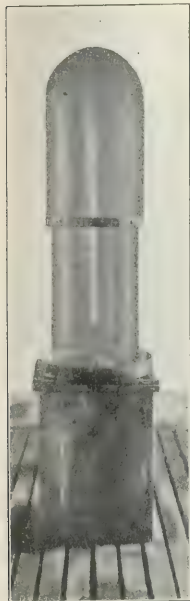
this bore by the Reservation Commission in order to restore the flow.

It was found upon careful investigation that the bore was very crooked and irregular and was filled to

June, 1912, and an excellent spring, spouting many feet above the level of the flow, was secured. This revival was brought about by placing water columns on the two Champion springs which were wasting about

200 gallons per minute and seemed to be the key to the control of the mineral water basin. This spring was cleaned again in April, 1913, and now has a flow of about one gallon per minute. The water is strongly mineralized, being low in chlorides but high in sodium and magnesium bicarbonates. The water is an excellent table water and is served at the spring.

*Old Red Spring*—This spring is situated on Spring Avenue and was discovered in 1770 or about as soon as the locality was visited by white men, being the next spring found after the discovery of the famous "High Rock." In 1784, the first bath house was erected on the property. From that time up to the acquirement of the spring by the Reservation Commission several bath houses had been built on the site of the old one and various improvements were made in the spring. The flow for many years was sufficient to maintain the baths and allow the water to be bottled. The spring had a reputation for the great curative properties of its water and was a famous resort in the days of Saratoga's popularity. When the state took over this property the bath houses, bottling house and equipment were old, crude and unsuitable for continuance under State ownership so the buildings were taken down. The spring itself was also in bad condition, the wooden tubing being neither sanitary nor permanent. In July, 1912, it was decided to retube the spring, and



GEYSER SPRING

to avoid excavating an eight inch steel casing was inserted into the wooden tubing, and the space between the two packed with concrete. After retubing, the natural flow was slightly greater than before but was not enough to meet the demands for bathing or bottling without resorting to pumping. The spring is 22 feet deep and has a flow of about one quart per minute. The water is moderately mineralized averaging with that of the Columbian. It is one of the famous iron springs and derived its name from the red coloration due to iron which the water contained.

*The New Red Spring* is situated on this same property about 100 feet southeast of the Old Red Spring. It was drilled in 1885 and is 60 feet deep. The water of this spring is high in iron content and is served to the public. It has a flow of about two quarts per minute and in mineralization it approaches the Washington.

*Washington Spring*—This spring is situated on South Broadway just above Congress Park in the old Clarendon Hotel property. It was discovered in 1806 and is 170 feet deep. The water does not flow at the surface of the ground but is obtained by pumping. The spring

had a celebrated reputation for its iron content and was used to a great extent. The property does not belong to the Commission but is owned by the St. Peters Catholic Church. Various scientific observations, which have been taken, show an improvement in this spring.

*The Columbian Spring* is located in the famous Congress Park, just west of the park entrance and on Broadway. It is one of the oldest mineral springs having been opened by a pioneer, Gideon Putman, in 1806. This is also a chalybeate water being closely connected with the Washington Spring as like changes in water levels are recorded simultaneously in both springs.

In April, 1913, the wooden tubing was cleaned and an iron casing inserted in it so as to insure sanitary conditions. The spring is eleven feet deep and its waters are moderately mineralized.

STATE HYGIENIC LABORATORY  
ALBANY, NEW YORK

### THE DETERMINATION OF HARDNESS IN NATURAL WATERS

By CLARENCE BAHLMANN

Received December 1, 1913

Lime hardness, magnesium hardness, and total hardness constitute the three primary determinations in industrial water analyses. An alkalimetric method for total hardness by use of soda reagent is described in the American Public Health Association's Standard Methods of Water Analysis. Mention is made that errors due to solubility of the precipitated calcium and magnesium salts are not entirely obviated in this method, and that the most accurate figure for total hardness is that computed from the results for calcium and magnesium. This is true when these bases are determined gravimetrically, but when the magnesium is determined by Pfeifer and Wartha's lime water method as described in the 1905 edition of Standard Methods, the results are unsatisfactory. For this reason undoubtedly, this method has not been inserted in the 1912 edition of the above publication; in fact no volumetric method is given for either calcium or magnesium.

For many industrial purposes, rapidity in arriving at results is preferred to extreme accuracy, and simple volumetric methods are entirely satisfactory for ordinary purposes provided the deficiencies and limits of accuracy of the method are known. This paper is a summary of an investigation to ascertain the accuracy of results obtained by certain volumetric procedures for calcium, magnesium and total hardness. The tests were made upon fifteen samples of natural waters obtained from nearby rivers, springs and wells, and showing wide ranges in calcium and magnesium content as well as in organic matter.

#### CALCIUM HARDNESS

The ease of manipulation and accuracy of the permanganate titration of calcium oxalate suggests its applicability in water analysis. Depending upon the hardness of the water, volumes of 100 cc. to 500 cc. will give workable precipitates. Fifteen waters ranging

in lime hardness from 33.8 to 360.5 parts per million  $\text{CaCO}_3$  were examined. In only one instance did the volumetric result vary from the gravimetric by more than 2.5 parts per million  $\text{CaCO}_3$ ; the average variation for the 15 samples was only 1.2 parts per million. The greatest percentage error was 3.2 per cent and, as an average, 99.6 per cent of the gravimetric results was found by the volumetric procedure. These results are in entire accord with those reported by R. B. Dole,<sup>1</sup> who states that it is possible to estimate calcium volumetrically to within 1 part per million (2.5 parts per million  $\text{CaCO}_3$ ).

#### MAGNESIUM HARDNESS

The principle of Pfeifer and Wartha's method<sup>2</sup> for magnesium is that when lime water is added to a neutral solution of calcium and magnesium salts, the calcium salts remain unaltered while those of magnesium are precipitated as hydroxide, the lime water consumed being a measure of the magnesium present. The waters tested ranged in magnesium hardness from 15 to 295.6 parts per million, expressed as an equivalent amount of  $\text{CaCO}_3$ .

The same volume of lime water was added to all of these waters, and consequently the percentage of the added lime water consumed in the reaction increased as the magnesium hardness increased. If the accuracy of this method depends solely upon excess of precipitant, then we should expect the results to approach nearer to the true figures as the percentage of the lime water consumed in the reaction is decreased. The results, however, showed no relation whatsoever between excess of precipitant and accuracy of the volumetric results. On 4 samples (magnesium content from 15.0 to 20.9 p. p. m.) the percentage of added lime water theoretically needed to precipitate the magnesium varied only from 2.8 per cent to 3.9 per cent, yet the volumetric results ranged from 60 per cent to 86.1 per cent of the gravimetric amounts. Of two samples of practically the same magnesium content (21.8 and 23.0 p. p. m.), the volumetric result was in one case 82.6 per cent and, in the other, 113 per cent of the true figure.

The magnesium hardness was determined twice on 6 of the samples, using 25 cc. and 50 cc. of the lime water. In this way the effect of varying excesses of precipitant upon the accuracy was studied when working with the same water. With 3 of these samples, the best results were obtained where the lesser percentage of lime water was theoretically required in the reaction, but with the other samples just the reverse was true. In the whole series, only 6 determinations gave results within 10 per cent of the correct figures, and these showed a variation in the percentage of added lime water theoretically needed of from 6.1 per cent to 57.6 per cent.

An excess of lime water is undoubtedly necessary and, while further study upon waters of the same general character might reveal certain limits of excess giving optimum results, it appears from the above work that the amount of excess varies with the nature

of the water. Even under the best conditions, magnesium hydroxide is appreciably soluble, causing low results. Another factor involved is the presence and relative concentration of other dissolved salts and organic matter. It is needless to state that no reliance can be placed upon any procedure exhibiting discrepancies such as shown above by the lime water method for magnesium.

#### TOTAL HARDNESS

The range in total hardness of the 15 waters tested was from 48.8 to 655.5 parts per million in terms of  $\text{CaCO}_3$ . For waters of low or medium hardness 0.04 *N* soda reagent and 0.02 *N*  $\text{H}_2\text{SO}_4$  were used, with harder waters, 0.1 *N* soda reagent and 0.1 *N* acid. The original titer of the soda reagent in terms of standard acid was determined not only by direct titration but by a blank determination on distilled water conducted under conditions identical with those to which the sample was subjected. As an average, when basing the value of the soda reagent upon the direct titration, only 83.7 per cent of the gravimetric total hardness was found, but on the basis of the blank determination, 95.8 per cent of the true total hardness was found by the volumetric method. The necessity of making a control determination in all cases is therefore indicated.

The same volume of soda reagent was added to these waters and it follows that the percentage of added alkali consumed increased as the total hardness increased. When only 7.2 per cent of the precipitant was used up in the reaction, the volumetric result was 100.4 per cent of the gravimetric, and the percentage of the true amounts found by the volumetric method decreased in fairly regular amounts as the percentage of soda reagent required for the reaction increased. When as much as 79.7 per cent of the added alkali was consumed, only 76.8 per cent of the gravimetric total hardness was obtained by the volumetric method.

It is evident from the above that low results are to be attributed to insufficient excess of the precipitant. Several of the samples, on which 50 cc. of 0.04 *N* soda reagent had been used, were examined again, using 25 cc. of 0.1 *N* soda reagent. This trial indicated that the best result on any one sample was always obtained where the largest excess of alkali was present. Twenty-five determinations were made upon the 15 waters and all results were within 5 per cent of the true figures when not over 35 per cent of the soda reagent was consumed in the reaction. The relationship existing between the percentage of added soda reagent theoretically required in the reaction and the accuracy of the volumetric result for total hardness is shown in the following table:

Per cent of added soda reagent theoretically required	No. of determinations	Average per cent of gravimetric total hardness found by volumetric method
0-10	2	100.4
10-20	6	99.1
20-30	4	97.5
30-40	4	96.3
40-60	4	94.1
60-80	5	89.1

It appears from this table that the best volumetric

<sup>1</sup> Geological Survey, *Water Supply Paper* 236, 28.

<sup>2</sup> *Z. anal. Chem.*, 1902, 199.



results are obtained when the soda reagent is added in such quantities that not more than 20 per cent of it enters into the reaction, and that the results are within 5 per cent of the true amounts when not more than 40 per cent of the alkali is used up.

#### MAGNESIUM HARDNESS BY DIFFERENCE

It has been shown that the soda reagent method for total hardness is quite satisfactory for ordinary work if care be taken to have sufficient excess of the alkali present, and that the permanganate titration for calcium is very accurate. When the magnesium is computed by difference, it suffers from the errors of the 2 direct methods and low results are to be expected because the total hardness figures are themselves low, due to the appreciable solubility of normal calcium carbonate and magnesium hydroxide. With certain waters, however, very close results can be obtained by this method. Seven of the samples, showing a range in hardness encountered in the Ohio River at this locality (48 to 130 p. p. m. total hardness; 15 to 37 p. p. m. magnesium hardness), gave very satisfactory results for magnesium by difference, the average percentage of the true amount being 98.6 per cent. With waters ranging in total hardness from 136 to 655.5 p. p. m. and in magnesium hardness from 63.8 to 295.6 p. p. m., however, the average accuracy was but 90.3 per cent. In such hard waters a comparatively small percentage error in the total hardness affects the magnesium to a greater extent, especially if the sample contains a relatively small quantity of this base in comparison to the lime content.

It appears then, that with comparatively soft waters a procedure, whereby the total hardness and calcium hardness are determined volumetrically as outlined, above and the magnesium by difference, is satisfactory for ordinary purposes. This method can also be applied to hard waters the general character of which is familiar to the analyst, provided he applies a correction factor determined by occasional comparisons of the volumetric with gravimetric results. Hard waters very low in magnesium as compared to calcium content will give the least satisfactory results, and the gravimetric method for magnesium must be resorted to in this case if accurate figures are desired.

#### SUMMARY

I. No volumetric methods for calcium or magnesium are given in the 1912 edition of Standard Methods of Water Analysis.

II. For ordinary purposes, rapidity is preferred to extreme accuracy, and volumetric methods are desired.

III. The estimation of calcium by titration with permanganate is easily and quickly performed and the results are very accurate.

IV. The estimation of magnesium with lime water is entirely unreliable.

V. The best results for total hardness are obtained when less than 20 per cent of the soda reagent is used up in the reaction, and the results will be within 5 per cent of the true amount when not more than 40 per cent of the soda reagent is consumed. The original

strength of the soda reagent must be determined by a blank determination.

VI. An ordinarily satisfactory procedure for examination of waters of low or medium hardness consists in determining the total hardness with soda reagent, the lime hardness with permanganate and ascertaining the magnesium content by difference. This method can also be used for hard waters by applying a correction factor. For very hard waters containing only small amounts of magnesium, this base must be determined gravimetrically if accurate results are desired.

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#### THE QUANTITATIVE ESTIMATION OF THE SALT-SOLUBLE PROTEINS IN WHEAT FLOUR

By GEO. A. OLSON

Received October 2, 1913

It has been repeatedly pointed out<sup>1</sup> that the strengths of alcohol suitable for the extraction of gliadin from flour, extracts other proteins besides gliadin. That this is unquestionably true was brought out by the writer in a previous article<sup>2</sup> on the estimation of gliadin in flour and gluten where it was found that the direct method for the extraction of the alcohol-soluble proteins gave considerably higher yield of nitrogen (38.3 per cent more) than could be obtained by either the indirect or coagulation methods.

Likewise it has been found<sup>3</sup> that 1 per cent sodium chloride extracts, besides edestin, leucosin and amino bodies, and some gliadin. Osborne<sup>4</sup> states that gliadin is practically insoluble in 10 per cent sodium chloride. From a quantitative point of view, it appears reasonable that a 10 per cent salt solution is the proper strength to use. But we find that a 10 per cent salt solution is impractical to work with owing to the large amount of salt present, and for this reason Teller,<sup>5</sup> and subsequently others, adopted strengths less objectionable. It was admitted by Teller and confirmed later by others by indirect methods that gliadin is partly soluble in 1 per cent salt solution, but just how soluble gliadin is no one has stated, nor even corrected for, when using this strength solution. A correction has been made for amide bodies by assuming that amide bodies are not precipitated by phosphotungstic acid. In the article referred to, the writer has pointed out the method for the estimation of the gliadin extracted by a 1 per cent salt solution and in connection with this the following experiments were conducted with the view of establishing a correct method for the estimation of edestin and leucosin proteins in flour.

Three different methods of procedure were adopted for the estimation of the salt-soluble proteins in flour. The first series of results was obtained by the method which is annually recommended to be followed by the

<sup>1</sup> U. S. Dept. of Agr., Bur. of Chem., *Bull.* No. 81 and 90.

<sup>2</sup> *This Journal*, 5, 917.

<sup>3</sup> *Ark. Bull.* No. 63; U. S. Dept. Agr., Bur. of Chem., No. 81 and No. 90.

<sup>4</sup> "The Proteins of the Wheat Kernel."

<sup>5</sup> *Ark. Bull.* No. 63.

referee on vegetable proteins for the A. O. A. C.<sup>1</sup> with a view to its final adoption. The second series of results was obtained from a modified method of the first where the coagulable nitrogen was considered. The third series of results was obtained from a still further differentiation than that given in the second method in that the alcohol-soluble in the salt-soluble which is coagulable was considered. Besides this a series of results are given according to Method III where for comparison a 10 per cent sodium chloride solution was used instead of the 1 per cent solution.

Method I—Instead of using 5 g. of flour and 250 cc. of one per cent salt solution twice the amount was used. The mixture was shaken at intervals of 5 minutes for the first two hours and then let stand for 24 hours when filtered clear. Nitrogen determinations in the total and phosphotungstic acid precipitates were made and the difference between these two determinations was regarded as amide nitrogen. The results were as follows:

TABLE I—1 PER CENT SALT SOLUBLE NITROGEN IN FLOUR (PERCENTAGES)

Number	Total N	Precipitated N	Amide N
O. C. ....	0.43	0.39	0.04
R. W. B. ....	0.38	0.29	0.09
B. L. ....	0.33	0.30	0.03
P. ....	0.50	0.41	0.09
L. C. ....	0.34	0.31	0.03
M. 15. ....	0.40	0.36	0.04

The larger part of the nitrogen carrying bodies soluble in 1 per cent salt solution are precipitated by phosphotungstic acid. In the proposed method there is no differentiation made between the gliadin and edestin and leucosin nitrogens soluble in 1 per cent salt solution.

Method II—Instead of precipitating the salt-soluble proteins with phosphotungstic acid directly, aliquots of the salt-soluble were boiled down to within 20 cc. of liquid. The precipitate formed was filtered off and washed with water. The resulting filtrate was then treated with sufficient phosphotungstic acid, thoroughly mixed and allowed to stand one hour, when the resultant precipitate was removed and washed with water containing phosphotungstic acid. Nitrogen determinations were made in the total and the two precipitates. The difference of the sum of the nitrogens from these precipitates and the total nitrogen was reckoned as amide nitrogen. According to this method of procedure, the following results were obtained:

TABLE II—DIFFERENTIATION OF THE COAGULABLE NITROGEN IN 1 PER CENT SALT-SOLUBLE (PERCENTAGES)

Number	Total N	Coagulable N	Pptd. N	Amide N
O. C. ....	0.43	0.130	0.250	0.050
R. W. B. ....	0.38	0.045	0.230	0.105
B. L. ....	0.33	0.055	0.240	0.035
P. ....	0.50	0.125	0.275	0.100
L. C. ....	0.34	0.120	0.230	0.000
M. 15. ....	0.40	0.065	0.270	0.065

Since gliadin is appreciably soluble in 1 per cent salt solution, one would expect to find this material included with what has been generally estimated as albumin and globulin. The resulting data given in Table II do not show what portion of the nitrogenous

bodies are gliadin bodies. Method II is better for the separation of the protein bodies soluble in one per cent salt solution than Method I, because the nitrogenous bodies coagulable by heat are separated from those not coagulable. The amounts of amide nitrogen obtained by difference in this method are practically identical with the amounts obtained in Method I.

The writer found in earlier investigations that it was possible to separate gliadin from the other salt-soluble proteins, and as a result of these investigations the following method for the estimation of the edestin and leucosin fractions in flour was adopted.

Method III—200 cc. aliquots of salt-soluble (10 grams of flour digested with 500 cc. of 1 per cent sodium chloride) were boiled down to within 20 cc. of liquid, then slowly evaporated to dryness on an iron hot plate. The solid was digested with 100 cc. of 55 per cent alcohol<sup>1</sup> by volume, filtered, then washed with same strength alcohol. The precipitate obtained was regarded as albumin. The alcohol filtrate was evaporated to within 10 cc. and 50 cc. of water added, boiled down to 35 cc., 15 cc. more water added, allowed to cool to room temperature and then filtered. The coagulum was washed with cold distilled water and reckoned as gliadin nitrogen. The coagulum filtrate was precipitated with phosphotungstic acid and reckoned as globulin nitrogen. The sum of the nitrogens obtained in the precipitates deducted from the total nitrogen leaves a small amount of unaccounted-for nitrogen which may be regarded as amide nitrogen. In Table III are given the results found according to this method.

TABLE III—INCLUDES THE ESTIMATION OF THE GLIADIN NITROGEN IN 1 PER CENT SALT-SOLUBLE (PERCENTAGES)

Number	Total N	Coag. N Insol. in alcohol	Gliadin N	Pptd. N	Amide N
O. C. ....	0.43	0.070	0.100	0.190	0.070
R. W. B. ....	0.38	0.080	0.095	0.140	0.065
B. L. ....	0.33	0.060	0.115	0.125	0.030
P. ....	0.50	0.125	0.160	0.165	0.050
L. C. ....	0.34	0.075	0.135	0.130	0.000
M. 15. ....	0.40	0.080	0.085	0.175	0.060

According to the results found and recorded in Table III it will be noted that the largest amount of nitrogen material soluble in 1 per cent salt solution was precipitated by phosphotungstic acid, which is nearly double that found in the coagulable insoluble in alcohol. The per cent of the alcohol-soluble which is coagulable is as much or more than the amount of nitrogen material insoluble in alcohol. In other words, there is very little nitrogen material extracted with 1 per cent salt solution that is not soluble in 55 per cent alcohol by volume.

In another series of experiments the same flours were digested with 10 per cent sodium chloride instead of 1 per cent solution. The method of procedure for the separation of the different nitrogen bodies was the same as that given in Method III. Owing to the large amount of salt present the alcohol separation method was tedious and slow. The various fractions for the nitrogen bodies soluble in 10 per cent salt solution are recorded in Table IV.

<sup>1</sup> See proceedings of Association, issued as bulletins, Bureau of Chemistry, Department of Agriculture.

<sup>2</sup> Fifty per cent alcohol is just as efficient as alcohol of higher strengths.

TABLE IV—INCLUDES THE ESTIMATION OF THE GLIADIN NITROGEN IN 10 PER CENT SALT-SOLUBLE (PERCENTAGES)

No.	Total N	Coag. N insol. in alcohol	Gliadin N	Pptd. N	Amide N
O. C.	0.290	0.215	0.015	0.043	0.017
R. W. B.	0.210	0.175	0.010	0.005	0.020
B. L.	0.160	0.125	0.005	0.025	0.005
P.	0.310	0.268	0.010	0.020	0.012
L. C.	0.220	0.165	0.023	0.008	0.024
M. 15.	0.260	0.203	0.007	0.040	0.010

As would naturally be expected, the per cent of nitrogen extracted with a 10 per cent salt solution is considerably less than that extracted with a 1 per cent salt solution. The reason for a much lower yield of nitrogen bodies is due to the increased concentration of the solute. It will be noted from the data given in Table IV that there is very little nitrogen material extracted which is soluble in 55 per cent alcohol by volume, and about 80 per cent of the total proteins soluble in 10 per cent salt solution are coagulated upon boiling down or increasing the salt concentration.

When the data for the total nitrogen and the various fractions obtained in the 1 per cent salt extraction are compared with those obtained in the 10 per cent salt extraction (see data in Tables III and IV), it will be noted that the amount of nitrogen material separated varies in any one group, depending upon the concentration of the solvent used for extracting these bodies. In the one case it is found that there is considerable gliadin and phosphotungstic acid precipitated nitrogen extracted, while in the other only a limited quantity is found which is not directly coagulable upon boiling the solution. The large amount of nitrogen bodies extracted by 10 per cent salt solution insoluble in 55 per cent alcohol by volume are insoluble in this strength of alcohol, owing to the concentration of the salt present. In Table V the sum of the figures given in Tables III and IV for alcohol insoluble and phosphotungstic acid precipitated nitrogen are compared with each other. In addition the total nitrogen in the 10 per cent salt solution with the gliadin correction has been included.

TABLE V—RESULTS FOR ALCOHOL INSOLUBLE AND PRECIPITATED NITROGEN IN 1 AND 10 PER CENT SALT-SOLUBLE (PERCENTAGES)

No.	1 Per cent NaCl	10 Per cent NaCl	
	Alcohol insol. and pptd. N	Alcohol insol. and pptd. N.	Salt-sol. N — gliadin N
O. C.	0.260	0.258	0.275
R. W. B.	0.220	0.180	0.200
B. L.	0.185	0.150	0.155
P.	0.290	0.288	0.300
L. C.	0.205	0.173	0.197
M. 15.	0.255	0.243	0.253

Having a method for estimating the gliadin nitrogen that may be extracted from wheat or its product by salt solution, it will be noted from the data presented in Table V that the amount of edestin and leucosin nitrogen is the same whether the concentration of sodium chloride be 1 or 10 per cent, providing the gliadin nitrogen is accounted for.

Referring again to the data given in Tables III and IV, it will be noted that the amount of nitrogen insoluble in 55 per cent alcohol in the 1 per cent salt extract is quite small and that of the nitrogen bodies precipitated by phosphotungstic acid is very large, while in

case of the 10 per cent salt solution the per cent alcohol insoluble nitrogen is very large while only a noticeable amount of nitrogen is found in the phosphotungstic acid precipitate. These facts naturally raise the question, Are we dealing with true globulins and albumins? The quantitative data obtained and the method of procedure followed indicate that the substances spoken of as globulin and albumin are only such in 10 per cent sodium chloride solution, while in lower per cents of sodium chloride there is a smaller quantity of such material.

Again, if the substances extracted from flour with 10 per cent salt solution are globulin and albumin, then either one or both of these two materials in less concentrated salt solution, or water, are wholly soluble or partly soluble in 55 per cent alcohol or alcohol of higher strengths. This thought has weight in the preceding article on the estimation of the gliadin nitrogen in flour where it was found that approximately 68 per cent of the alcohol-soluble was coagulable by the direct method and corroborated in the indirect method of procedure and subsequent analyses. The data given for the alcohol-soluble uncoagulable nitrogen, where different strengths of alcohol were used, should also be considered in connection with this view.

There is sufficient reason to believe that the globulin and albumin of wheat are appreciably soluble in diluted alcohols even in the presence of 1 per cent sodium chloride solution. And since gliadin is appreciably soluble in 1 per cent salt solution, the methods that have been followed in the past where 1 per cent salt solution is used, includes gliadin as a part of globulin and albumin nitrogen and in the direct alcohol extraction of flour albumin and globulin are included as a part of the gliadin nitrogen. With 10 per cent salt solution only a very small part of the gliadin nitrogen is considered.

The amount of gliadin nitrogen extracted in salt solution depends upon the amount of salt used, being approximately 90 per cent more in a 1 per cent sodium chloride solution than was found to be the case in 10 per cent sodium chloride. The fact that the gliadin nitrogen can be removed from the salt solution regardless of the strength of salt used up to and including 10 per cent sodium chloride, makes the 1 per cent salt extraction method, owing to the more rapid filtering, more rapid digestion, etc., the most desirable one to follow. Omitting the determination for gliadin nitrogen and making the one for amide nitrogen in its place, renders the method of procedure for the estimation of edestin and leucosin nitrogen less difficult and is as follows:

Digest 10 grams of flour with 500 cc. of 1 per cent sodium chloride solution, shaking at intervals of 5 minutes for the first two hours, then allow to stand over night in a cool place. Filter clear and use aliquots of 200 cc. each. Boil to within 20 cc. of liquid; then slowly evaporate to dryness on iron hot plate. Digest the solid mass in each beaker with 100 cc. portions of 55 per cent alcohol by volume, filter, wash precipitate on filter paper with same strength alcohol. Determine nitrogen in this precipitate by the Kjeldahl method,



and after correcting for filter paper, etc., by blank determinations, the difference found should be regarded as albumin nitrogen.<sup>1</sup>

Evaporate the alcohol filtrate to within 10 cc., add 50 cc. of distilled water, boil down to 35 cc., then add 15 cc. more of distilled water, allow to cool to room temperature and filter. Wash precipitate with cold distilled water. Owing to the sticky nature of this material and the difficulty in transferring the same to the filter paper, it is not advisable to make this determination.

The resulting filtrate obtained in the gliadin separation is treated with sufficient phosphotungstic acid to cause precipitation of the albumin filtered and washed with distilled water containing phosphotungstic acid. Nitrogen determinations in this precipitate should be corrected for by running blanks containing filter paper washed in phosphotungstic acid. The nitrogen obtained by difference is regarded as globulin nitrogen.

The nitrogen found in the phosphotungstic acid precipitate filtrate when properly corrected for is considered amide nitrogen. The total nitrogen found as amide, globulin and albumin when deducted from the total salt-soluble nitrogen is gliadin nitrogen extracted in the 1 per cent salt solution.

#### CONCLUSIONS

1. One per cent sodium chloride extracts from flour edestin, leucosin and gliadin.

2. The amount of gliadin extracted by 1 per cent sodium chloride solution approximately amounts to about 29 per cent of the total proteins.

3. The amount of gliadin extracted by 10 per cent sodium chloride solution approximately amounts to about 5 per cent of the total proteins.

4. The gliadin nitrogen extracted by solutions containing sodium chloride can be determined and corrected for in making edestin and leucosin nitrogen estimations of flour and its products.

5. The amount of nitrogen bodies extracted with salt solutions and directly coagulated by heat varies with the concentration of the solvent. The 10 per cent concentration gives higher results than was found possible with a 1 per cent salt solution.

6. The nitrogen bodies soluble in salt solution are partly or wholly soluble in diluted alcohols varying with the concentration of the sodium chloride used.

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PULLMAN

#### AN INVESTIGATION OF THE PRESENCE OF FURFURAL IN CIDER VINEGAR

By AGNES A. ANDERSON

Received November 15, 1913

That pure cider vinegar contains volatile reducing substances has been known for some time and several methods have been given<sup>2</sup> for eliminating these substances in order to get the true amount of reducing sugars. The presence of furfural in these volatile reducing substances was discovered while doing routine vinegar analyses in the Kansas State Food Laboratory.

<sup>1</sup> Globulin does not coagulate at temperatures below 100° C. (see "Proteins of Wheat Kernel," Osborne, Carnegie issue, p. 116).

<sup>2</sup> THIS JOURNAL, 5, 845, 928.

Since nothing on the subject could be found in the literature an investigation was begun to determine its presence in normal cider vinegars. The results seem to warrant publication at this time.

Twenty-eight samples of cider vinegar of known purity were tested for furfural by the aniline acetate method as given by Leach.<sup>1</sup> Nineteen gave a positive test, nine being negative. These vinegars were made at the laboratory and their history known. In addition to these samples some farmers' vinegars were tested with similar results. From these results it is seen that furfural may be present normally in cider vinegars and its presence does not necessarily indicate added wood acetic acid.

In the *Abstract Journal* (7, 666) appeared a method by Ronnet for detecting added caramel in vinegar. This method is based upon the formation of furfural when sugar is heated in the process of making caramel, and makes use of the Fiehe resorcinol reagent.<sup>2</sup>

Since it appears that furfural is normally present in some cider vinegars, its presence can again be said not to indicate adulteration from caramel. This test for caramel was applied to the vinegars of known purity and in every case an affirmative result was obtained. Four of the samples tested for caramel did not give a test for furfural upon distillation, but gave a very positive caramel test. This may be due to decomposition of the sugar during the drying on the water bath. The water bath was carefully maintained at a temperature below 70° C. to avoid this possible decomposition, so this fact adds to the unreliability of the method. Caramel was added to some of the vinegars, but the resulting tests were not different from those to which none had been added.

TABLE I

No.	Variety	Furfural	No.	Variety	Furfural
P1	Winesap Pomace...	Neg.	18	Gano.....	Aff.
P2	Pomace.....	Neg.	P18	Gano Pomace .....	Aff.
3	Jeteton.....	Neg.	19	Jeteton.....	Aff.
P3	Jeteton Pomace....	Neg.	20	Winesap.....	Neg.
6	Jeteton.....	Aff.	21	Jeteton.....	Neg.
7	Clayton.....	Aff.	22	Roman Beauty.....	Neg.
8	Black Twig.....	Aff.	23	Winesap.....	Aff.
9	York Imperial.....	Aff.	24	Black Twig.....	Aff.
10	Ben Davis.....	Aff.	25	Missouri Pippin.....	Aff.
P10	Ben Davis Pomace..	Aff.	A	Unknown.....	Aff.
12	Limbertain.....	Aff.		Pomace of above .....	Neg.
P13	Limbertain Pomace..	Aff.	70284	Farmers' Vinegar....	Aff.
14	Winter Greening....	Aff.		Rotten apples.....	Neg.
15	York Imperial.....	Aff.	70284A	Farmers' Vinegar....	Neg.
17	Winesap.....	Aff.	9373	Farmers' Vinegar....	Aff.
P17	Winesap Pomace....	Neg.	5159	Farmers' Vinegar....	Neg.

TABLE II

No.	Variety	Caramel	Furfural test*
A	Unknown.....	Good test	Aff.
9	York Imperial.....	Good test	Aff.
	York Imperial + Caramel.....	Good test	...
70284	Farmers' Vinegar.....	Good test	Aff.
5159	Farmers' Vinegar.....	Good test	Neg.
9373	Farmers' Vinegar.....	Good test	Aff.
	Rotten Apples.....	Good test	Neg.
70284A	Farmers' Vinegar.....	Good test	Neg.
21	Jeteton.....	Good test	Neg.

The above tables give the results; duplicate determinations are not included since in every case the results checked.

<sup>1</sup> Leach, "Food Inspection and Analysis," p. 777.

<sup>2</sup> Bur. of Chem., Bull. 154, 15.

## CONCLUSION

I. Pure cider vinegar may contain furfural as a natural constituent. Its presence, therefore, cannot be taken as indicating added wood acetic acid.

II. Since cider vinegars may contain furfural, its presence cannot be taken as indicating added caramel.

III. Cider vinegars may give a test for caramel by the Ronnet method without containing furfural or added caramel, hence the method is not reliable.

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## SOME ABNORMAL FACTORS OF SO-CALLED FARMERS' CIDER VINEGARS

By JOHN C. DIGGS

Received Nov. 19, 1913

The following analyses were made of eighteen samples of vinegar which were entered in an apple product exhibit of an apple show held in Indiana. Instructions relative to the exhibit were to the effect that only legal cider vinegars should be entered.

## ANALYSES OF VINEGARS

Lab. No.	Intensity of color	Pol. tube	Acidity	Total solids	Total sugars as invert	Non-sugar solids	Alcohol	Ash	Alk. of ash	Sol. P <sub>2</sub> O <sub>5</sub>	Insol. P <sub>2</sub> O <sub>5</sub>	Glycerine	Lead acetate ppt.	Ash Non-sugars
7604 B	Medium.....	-1.8	9.56	5.09	0.63	4.46	2.91	0.757	52	16.8	36.2	0.51	Medium	1. 5.9
7605 B	Light.....	-1.6	3.73	9.64	5.97	3.67	0.61	0.460	34	10.9	19.4	0.44	Medium	1. 7.9
7606 B	Very light.....	0.0	1.55	2.07	0.05	2.02	2.62	0.265	18	8.5	20.1	0.39	Light	1. 7.6
7607 B	Light.....	+4.0	3.66	3.22	1.54	1.68	1.96	0.304	20	13.5	28.5	0.12	Light	1. 5.5
7608 B	Very dark.....	0.0	8.23	2.06	0.35	1.71	2.16	0.388	34	19.1	21.1	0.07	Light	1. 4.4
7609 B	Very dark.....	+1.4	3.92	1.73	0.78	0.95	0.35	0.358	22	5.8	30.8	0.30	Light	1. 2.6
7610 B	Medium.....	0.0	5.01	2.96	0.39	1.57	0.80	0.392	24	12.5	30.1	0.23	Medium	1. 4.0
7611 B	Dark.....	-0.8	5.15	3.16	1.01	2.15	0.31	0.409	16	11.2	30.1	0.25	Heavy	1. 5.2
7612 B	Medium.....	+0.4	2.50	2.60	0.16	2.44	0.32	0.272	20	11.7	14.5	0.22	Medium	1. 5.5
7613 B	Medium.....	-0.4	3.88	4.66	1.05	3.61	0.28	0.494	30	20.4	12.1	0.39	Heavy	1. 7.3
7614 B	Very dark.....	-0.6	10.25	4.47	0.75	3.72	0.28	0.552	48	24.7	32.6	0.18	Heavy	1. 6.7
7615 B	Medium.....	-1.2	5.53	5.37	0.31	5.06	0.07	0.713	32	8.4	28.0	0.25	Light	1. 16.1
7616 B	Medium.....	-1.4	6.99	2.00	0.28	1.72	0.35	0.478	38	6.6	19.3	0.32	Medium	1. 3.6
7617 B	Medium.....	-1.4	5.83	2.97	0.59	2.38	2.19	0.434	32	11.4	26.0	0.40	Medium	1. 5.5
7618 B	Dark.....	-3.8	6.32	2.57	0.69	1.88	0.35	0.293	26	10.8	25.0	0.42	Light	1. 6.4
7619 B	Medium.....	0.0	1.94	2.83	0.34	2.19	3.40	0.349	26	15.3	39.5	0.33	Heavy	1. 6.2
7620 B	Very dark.....	-2.8	4.38	3.04	1.15	1.89	0.14	0.506	46	26.8	34.9	0.31	Heavy	1. 3.7
7621 B	Medium.....	-2.2	4.60	3.75	1.26	2.49	0.17	0.387	44	15.8	30.8	0.06	Heavy	1. 6.4
	Minimum.....	+4.0	1.55	1.73	0.05	0.95	0.07	0.265	16	6.6	14.5	0.06	Heavy	1. 2.6
	Maximum.....	-3.8	10.25	9.64	5.97	5.06	3.40	0.757	52	26.8	39.5	0.51		1. 16.1
Average.....		-0.64	5.13	3.53	0.96	2.47	1.28	0.411	31	16.6	27.7	0.28		1. 6.1

In color the vinegars ranged from a pale yellow to a reddish brown. The bouquets of a few were excellent while in some they were practically that of dilute acetic acid.

In general the methods of analysis were those given in Bulletin 137, Bureau of Chemistry, Dept. of Agriculture. The total sugars were determined by inverting the solutions and determining the reducing sugars. Alkalinity of the ash is expressed in cubic centimeters of N/10 acid for ash of 100 cc. sample. Phosphoric acid is expressed in milligrams of phosphoric acid in 100 cc. The other factors are in grams per 100 cc.

## DISCUSSION OF ANALYSES

The variation of the factors was remarkable. Many of these can be explained only as the result of tampering—the addition of some foreign material, dilution with water, or both.

The polarization in the 200 mm. tube ranged from +4.0° V. to -3.8° V. The positive readings undoubtedly indicated the addition of sugar or glucose.

The acid content varied from 1.55 to 10.25 grams per 100 cc. The higher acid samples are impossible figures and indicate the addition of acetic acid. The lower acid values indicate dilution with water or insufficient fermentation. The total solids range from 9.64 grams, a sample very high in sugar, to 1.73 grams per 100 cc. In one sample the sugars were as high as 5.97 grams and in another as low as 0.05 gram per 100 cc. The sample having 5.97 grams of course has not been properly fermented—the alcohol fermentation having been arrested by the addition of vinegar. The highest non-sugar solid content was 5.06 grams per 100 cc. Such a factor is impossible from an apple cider and has been caused by the addition of some foreign material. Just why any one should wish to make such a concoction is a puzzle. The highest alcohol value was 3.4 grams per 100 cc. Any alcohol value above 0.6 per cent indicated that the fermentation was not as complete as it should have been. The ash of all came within the limit of the law, the highest being 0.757, the lowest 0.265 gram per 100 cc. The alkalinity

of the ash varied from 16 to 52 cc. of tenth normal acid per 100 cc. sample. Eight samples were below 30 the legal minimum. The soluble phosphoric acid ranged from 6.6 mgs. to 26.8 mgs. per 100 cc. Five samples were below 10 mgs. per 100 cc., the legal standard. The glycerine content varied from 0.51 gram to 0.06 gram per 100 cc. A fully fermented cider will contain not less than 0.25 gram of glycerine and a sample containing less than that amount is not a true cider vinegar. The ratio between the ash and non-sugars should be close to 1 : 5. However, we find the ratio 1 : 16.1 for the highest and 1 : 2.6 as the lowest.

From these analyses we would call Sample 7604 fraudulent. It contains 9.56 grams of acetic acid and nearly three grams of alcohol per 100 cc., an impossible condition. Sample 7605 is slightly low in acid but has nearly six grams of unfermented sugar, indicating incomplete alcoholic and acetic fermentation. The deficiencies of Samples 7606, 7607, 7611, 7613, 7619,

7620 and 7621 are probably due to a similar cause. However, the glycerine content and alkalinity of the ash of some of these samples would indicate that they have been tampered with. Samples 7610 and 7611 have probably been watered.

#### SUMMARY

The results of these analyses show the uncertainty of unscientific methods in the manufacture of vinegar.

Pernicious practices exist among farmers who put vinegar on the market.

Fraudulent vinegars are often sold as farmers' cider vinegars.

L. LABORATORIES OF THE INDIANA STATE BOARD OF HEALTH  
INDIANAPOLIS

### THE ANALYSIS OF MAPLE PRODUCTS. III

#### The Range of Variation of Analytical Values in Genuine Maple Syrups

By J. F. SNELL AND J. M. SCOTT

Received January 5, 1914

In Paper II of this series<sup>1</sup> it was pointed out that the usefulness of a method for the detection of the adulteration of maple syrup with pure sucrose (or with granulated sugar) depends upon two factors: (1) The limits of natural variation of the analytical value in question in genuine maple syrups; (2) the rate at which the value falls off as the proportion of genuine syrup in the mixture decreases. It was shown that in respect to the latter factor, the Canadian lead method has a decided advantage over any of the other methods. While the ash values and the Winton lead number, as determined by the original Winton method or by Ross's modification thereof, fall off approximately in proportion to the amount of genuine maple syrup, the Canadian lead number falls off at a much more rapid rate, and reaches zero in mixtures containing as much as twenty per cent of genuine syrup. But it was shown that this apparent advantage of the Canadian method is, to a large extent, counteracted by the wide range of variation shown by this value in genuine syrups.

The electrical conductivity value, determined as described in the first paper of the series,<sup>2</sup> resembles the total ash and the Winton lead value rather than the Canadian lead value. Its rate of fall is in general a little less than proportional to that of the maple syrup content, but its range of variation expressed in percentage of the minimum is less than that of any of the other values studied in Paper II.

The objects of the present communication are three: (1) To report the results of the analysis of 126 genuine Canadian syrups of the season of 1913. (2) To study in more detail than in Paper II the ranges of variation of the analytical data in genuine syrups, with reference to the aforesaid results and to those of Bryan,<sup>3</sup> Jones,<sup>4</sup> and McGill.<sup>5</sup> (3) To propose a scheme for the detection of adulteration with sucrose

less laborious and more effective than those commonly used.

#### SOURCE AND COLLECTION OF THE SAMPLES

The territory from which our syrups were collected extends from Lake Huron to the southeastern boundary of the Province of Quebec and is, we think, fairly representative of the chief maple-producing districts of the Dominion of Canada. By province and county the sources of the syrups are as follows, the total number<sup>1</sup> from Ontario being 57, that from Quebec 69:

Serial numbers	Province	County	Serial numbers	Province	County
1-13	Quebec	Argenteuil	71-88	Quebec	Stanstead, Compton and Sherbrooke
14-23	Ontario	Carleton	89-94	Ontario	Elgin and Middlesex
24-31	Ontario	Middlesex and Oxford	95-99	Ontario	Grey and Bruce
32-41	Ontario	Simcoe	100-117	Quebec	Huntingdon
42-61	Quebec	Shelford, Brome and Missisquoi	118-122	Ontario	Frontenac
62-70	Ontario	Grey	123-126	Ontario	Dufferin, Wellington and Peel

The syrups represent, we think, the most varied conditions of soil and elevation, and of method of manufacture to be found in the territory in question.

In the collection of the syrups we made it a point to reduce to a minimum the danger of including any adulterated samples. Samples 1-13 were collected by the senior author in person. The other samples from the Province of Quebec were collected by the Macdonald College Demonstrators resident in the respective districts, who were instructed to take the samples direct from the woods under such conditions as to preclude the possibility of adulteration. The samples from the Province of Ontario were collected by the District Representatives of the Ontario Department of Agriculture, who are graduates of the Ontario Agricultural College, acting as local agricultural demonstrators and referees. The same instructions were issued to these gentlemen as to the Macdonald College Demonstrators and we have their personal assurances that the instructions were strictly observed. Our thanks are due to them for their kind coöperation and to the Hon. James Duff, Minister of Agriculture for the Province of Ontario, for permitting us to ask this service of the Representatives of his Department.

#### THE RESULTS OF ANALYSIS OF THE SAMPLES

In addition to the analytical results, we have information about the method of manufacture of each syrup, including the kind of evaporator, the kind of filter, the clarifying agents used and whether the syrup had been allowed to settle or not. Table I reports 23 typical syrups.

**Moisture**—The per cent of moisture is derived from the refractometer reading by use of the tables of Prinsen Geerligs as given by Bryan.<sup>2</sup> The refractometer used was the Féry instrument made by Adam Hilger, London, England. With this instrument, using sodium light, we found it possible to make

<sup>1</sup> Quebec produces 65 per cent, Ontario 32 per cent of the maple syrup and sugar of the Dominion of Canada.

<sup>2</sup> Bryan, *Jour. Amer. Chem. Soc.*, **30** (1908), 1445.

<sup>1</sup> Snell and Scott, *This Journal*, **5** (1913), 993.

<sup>2</sup> Snell, *This Journal*, **5** (1913), 740.

<sup>3</sup> Bryan, *Bur. Chem.*, U. S. Dept. Agr., *Bull.* **134** (1910).

<sup>4</sup> Jones, *Vermont Agr. Expt. Sta. Ann. Rep.*, **1904**, **5**, 315.

<sup>5</sup> McGill, *Lab. Inland Revenue Dept.*, Ottawa, *Bull.* **228** (1911).



TABLE I—SELECTED ANALYSES OF PURE CANADIAN MAPLE SYRUPS OF SEASON OF 1913

TABLE 1.—ANALYSIS OF PURE CANNED SYRUPS.																		
NO.	EVAPORATOR	FILTERING MATERIAL	CLARIFICATION		REFRACTOMETER		MOISTURE—Per cent	PERCENTAGE ASH			ALKALINITY OF ASH		LEAD NUMBERS		ACID VALUE	CONDUCTIVITY VALUE		
			Clarifying agent	Setting	Reading	Temp., ° C.		Total	Sol	Insol	SOL. ASH	INSOL. ASH	Sol	Insol			Canadian	Modified Winton
3	Patent	Felt	None	Settled	1.4583	21.0	32.84	0.76	0.49	0.27	1.81	66	64	1.03	2.16	1.87	0.70	131
24	Patent	Cloth	None	Settled	1.4457	27.0	37.83	0.97	0.55	0.42	1.31	84	130	0.65	4.25	2.53	0.85	159
29	Patent	None	None	Settled	1.4543	27.6	34.03	0.64	0.35	0.29	1.21	62	77	0.81	2.19	1.67	0.65	114
31	Patent	None	None	Not settled	1.4560	26.8	33.35	0.83	0.30	0.53	0.57	51	119	0.43	3.25	2.02	0.68	134
33	Kettle	Cheesecloth	Eggs	Settled	1.4527	23.7	35.04	1.39	0.77	0.62	1.24	102	148	0.69	6.01	3.17	1.03	230
36	Kettle	Flannel	Eggs	Settled	1.4459	24.8	37.90	1.24	0.71	0.53	1.34	103	150	0.69	5.01	3.06	0.89	205
37	Kettle	Cotton	Milk	Settled	1.4329	29.5	43.23	0.99	0.58	0.41	1.41	79	113	0.70	3.69	2.48	0.85	166
39	Kettle	Cotton	Milk	Settled	1.4436	29.4	38.54	1.27	0.65	0.62	1.05	88	150	0.59	5.51	2.91	0.91	204
40	Kettle	Flannel	Eggs	Settled	1.4581	22.0	32.86	1.01	0.65	0.36	1.81	101	92	1.10	3.90	2.73	0.38	183
43	Patent	Flannel	None	Settled	1.4566	23.0	33.39	0.62	0.35	0.27	1.30	59	69	0.86	1.88	1.55	0.41	112
44	Patent	Flannel	None	Settled	1.4569	29.0	32.82	0.61	0.45	0.16	2.81	65	48	1.35	1.98	1.41	0.70	123
61	Patent	Flannel	None	Settled	1.4328	26.0	43.56	0.74	0.35	0.39	0.90	60	98	0.61	3.01	1.83	0.56	130
81	Patent	Flannel	None	Settled	1.4534	24.6	34.66	1.01	0.43	0.58	0.74	66	145	0.46	4.92	2.86	1.06	159
89	Pans	Flannel	Eggs	Settled	1.4586	24.5	32.42	0.77	0.53	0.24	2.21	76	58	1.31	1.74	1.48	0.69	156
95	Iron pans	Cotton	None	Not settled	1.4441	22.5	38.92	1.47	0.55	0.92	0.60	87	195	0.45	7.50	3.43	1.27	202
96	Kettle	Cotton	Eggs, milk	Not settled	1.4303	23.2	44.88	1.58	0.76	0.82	0.93	102	201	0.51	7.24	4.09	1.46	219
100	Patent	None	Eggs, milk	Settled	1.4593	23.1	32.28	0.71	0.33	0.38	0.87	58	90	0.64	2.43	1.76	0.74	125
103	Patent	Felt	None	Settled	1.4298	28.6	44.70	1.21	0.45	0.76	0.59	81	150	0.54	5.83	3.08	1.02	168
105	Patent	Flannel	None	Settled	1.4602	22.0	31.97	0.85	0.64	0.21	3.05	78	76	1.03	3.02	2.23	0.76	149
115	Patent	Fine cloth	None	Settled	1.4471	22.2	37.55	0.83	0.41	0.42	0.98	59	114	0.52	3.56	2.20	0.97	134
121	Pans	Cotton	Eggs, milk	Settled	1.4575	23.2	33.03	1.25	0.64	0.61	1.05	97	137	0.71	6.22	3.19	1.01	195
124	Patent	Cheesecloth	Milk	Settled	1.4593	29.0	31.82	1.29	0.59	0.70	0.84	85	144	0.59	5.08	2.91	1.05	192
125	Kettle	Cheesecloth	Milk	Settled	1.4452	26.3	38.09	0.92	0.66	0.26	2.54	82	113	0.73	3.26	2.24	0.74	174
AVERAGE FOR 126 SYRUPS.....							34.24	0.88	0.48	0.40	1.20	68	116	0.59	3.48	2.30	0.75	147
MAXIMUM FOR 126 SYRUPS.....							44.88	1.58	0.77	0.92	1.61	103	201	1.35	7.50	4.09	1.46	230
MINIMUM FOR 126 SYRUPS.....							30.42	0.61	0.30	0.16	0.55	51	48	0.41	1.74	1.41	0.38	112

readings upon the darkest of our samples without dilution. We clarified them by filtering through cotton wool. The quantity filtered was about 25 cc. and the time required for the cold syrup to run through the filter was about 15 to 20 minutes. To satisfy ourselves that no error was introduced by evaporation during filtration we made readings upon three of the clearest syrups before, as well as after, filtering, and refiltered four other syrups, making readings before and after the second filtration. The results obtained in these experiments were as follows:

#### DRY MATTER CALCULATED FROM REFRACTOMETER READINGS—PERCENTAGES

CLEAR SYRUPS			REFILTERED SYRUPS		
No.	Before filtration	After filtration	No.	After 1st filtration	After 2nd filtration
1.....	63.26	63.15	1.....	66.97	67.04
2.....	67.16	67.31	2.....	62.92	62.87
3.....	55.12	55.06	3.....	67.06	67.20
			4.....	65.53	65.50

The St. Lawrence Sugar Refining Company of Montreal, through its Superintendent, Dr. C. Bardorf, courteously permitted us to make readings upon ten of the syrups with their Zeiss-Abbé refractometer for comparison with the results obtained with the Féry instrument. The results were as shown in Table II.

*Analytical Results*—All the data of Table I except the moisture are referred to dry matter.

The determinations of total, soluble and insoluble ash, of Canadian and modified Winton lead value, and of malic acid value were made according to the methods prescribed in the Canadian pure food stand-

ards,<sup>1</sup> not because these methods are in our opinion superior to others but because one of the objects of our investigation was to make a critical study of the standards for maple syrup adopted by the Canadian Government. As these determinations were made before we had obtained a refractometer, the quantity of syrup used in the lead number determinations was

TABLE II—COMPARISON OF REFRACTOMETERS

Sample	Abbé refractometer		Féry refractometer		
	Reading 20° C.	Corresponding dry matter	Reading	Temp. ° C.	Corresponding dry matter
1.....	1.4587	67.25	1.4570	28.7	67.16
2.....	1.4498	63.40	1.4483	26.2	63.26
3.....	1.4310	55.25	1.4298	28.6	55.30
4.....	1.4471	62.25	1.4459	24.8	62.10
5.....	1.4473	62.35	1.4457	27.0	62.17
6.....	1.4349	56.95	1.4329	29.5	56.77
7.....	1.4318	55.60	1.4303	23.2	55.09
8.....	1.4482	62.70	1.4470	27.8	62.83
9.....	1.4631	69.05	1.4609	31.0	69.03
10.....	1.4588	67.30	1.4574	28.5	67.34

that containing 5 or 25 grams of dry matter as estimated from the density. The results so obtained were afterwards recalculated to the basis of 5 or 25 grams dry matter, as determined by the refractometer. In the determinations of malic acid value the washing of the precipitate was continued to a filtrate volume of 100 cc., as it was found impracticable to wash "to freedom from soluble calcium salt," as indicated by testing with ammonium oxalate. The alkalinities of soluble and insoluble ash were determined in the usual manner.<sup>2</sup> The conductivity value determina-

<sup>1</sup> Canadian Order in Council G. 994, Nov. 8, 1911; McGill Lab. Inland Revenue Dept., Bull. 228 (1911), 5.

<sup>2</sup> Bryan, U. S. Dept. Agr., Bureau of Chem., Bull. 134 (1910), 17.

tions were made as described in Paper I of this series.<sup>1</sup>

TABLE III—COMPARISON OF CONDUCTIVITY VALUES AT 20° AND 25° C.

Conductivity			Conductivity		
No.	20° C.	25° C.	No.	20° C.	25° C.
1	202	230	11	113	129
2	195	219	12	112	127
3	181	205	13	107	121
4	180	204	14	107	121
5	180	202	15	108	121
6	168	197	16	105	120
7	172	195	17	98	116
8	169	192	18	94	115
9	160	183	19	103	114
10	155	177	20	99	112
Average	176.2	200.4		104.6	119.6
Difference		24.2	Difference		15.0
Diff. in % of value at 25° C.	12.1		Diff. in % of value at 25° C.	12.5	

It is difficult to draw any positive conclusions as to the relation of these analytical results to the district or to the method of manufacture of the syrup. In

and pans were used there to a much greater extent than patent evaporators and the practice of clarifying with eggs, milk or soda was very common. On the other hand the samples from Elgin County, although (with one exception) made in pans and treated with clarifying agents, do not show high values, and in Dufferin, Wellington and Peel Counties the single sample, No. 124, showing high values is one made with a patent evaporator, while the syrup made in a kettle, No. 125, although insufficiently evaporated shows low values throughout. Failure to evaporate to the proper density may in some instances, *e. g.*, Nos. 24, 37 and 103, account for high ash, lead values, malic acid value and alkalinity of insoluble ash, less calcium malate being forced out of solution than in the case of syrups concentrated to a sufficiently low moisture content to meet the Canadian standard (35 per cent). The same cause, together with others,

TABLE IV RANGE OF VARIATION OF ANALYTICAL DATA OF PURE MAPLE SYRUPS

	PERCENTAGE OF ASH				ALKALINITY OF ASH		ALKAL. SOL. ASH ALKAL. INSOL. ASH	LEAD NUMBER		MODIFIED WINTON LEAD NO.	MALIC ACID VALUE	CONDUCTIVITY VALUE	
	Total	Sol.	Insol.	SOL. ASH INSOL. ASH	Sol.	Insol.		Canadian	Winton				
MAXIMUM													
Bryan.....	1.68	1.23	1.01	3.86	122	208	1.83	...	4.41	...	1.60	...	
Jones.....	1.32	0.72	0.78	2.6	102	145	1.67	...	...	...	1.11	...	
McGill.....	1.38	0.79	0.75	...	...	...	...	...	6.56	2.38	...	1.16	...
Snell and Scott.....	1.58	0.77	0.92	3.61	103	201	1.35	...	7.50	...	4.09	1.46	230
MINIMUM													
Bryan.....	0.68	0.35	0.23	0.53	41	41	0.21	...	1.76	...	0.29	...	
Jones.....	0.77	0.45	0.25	0.7	46	55	0.45	...	...	...	0.65	...	
McGill.....	0.69	0.33	0.12	...	...	...	...	...	1.37	1.05	...	0.30	...
Snell and Scott.....	0.61	0.30	0.16	0.55	51	48	0.41	...	1.74	...	1.41	0.38	112
AVERAGE:													
Bryan.....	1.00	0.63	0.37	1.84	75	97	0.81	...	2.70	...	0.84	...	
Jones.....	0.92	0.58	0.34	1.78	79	83	0.98	...	...	...	0.82	...	
McGill.....	0.89	0.56	0.33	...	...	...	...	...	2.83	1.75	...	0.77	...
Snell and Scott.....	0.88	0.48	0.40	1.33	68	116	0.67	...	3.48	...	2.30	0.75	147
RANGE OF VARIATION EXPRESSED IN PERCENTAGE OF AVERAGE:													
Bryan.....	100	140	211	181	108	172	200	...	98	...	...	156	...
Jones.....	60	47	156	106	71	108	125	...	...	...	...	56	...
McGill.....	78	82	191	...	...	...	...	...	183	76	...	112	...
Snell and Scott.....	110	98	190	230	76	132	140	...	166	...	117	144	80
PERCENTAGE DEVIATION OF MAXIMUM FROM MEAN:													
Bryan.....	68	95	173	110	63	114	126	...	63	...	...	90	...
Jones.....	45	25	129	48	29	75	71	...	...	...	...	35	...
McGill.....	55	41	127	...	...	...	...	...	132	36	...	51	...
Snell and Scott.....	80	60	130	171	51	73	101	...	116	...	78	95	56
PERCENTAGE DEVIATION OF MINIMUM FROM MEAN:													
Bryan.....	32	44	38	71	45	58	74	...	35	...	...	66	...
Jones.....	16	22	26	61	42	34	54	...	...	...	...	21	...
McGill.....	23	41	64	...	...	...	...	...	52	40	...	61	...
Snell and Scott.....	30	38	60	59	25	59	39	...	50	...	39	49	24
PER CENT OF SAMPLES ABOVE MEAN:													
Bryan.....	42.8	42.6	38.0	46.2	42.8	42.6	44.9	...	46.6	...	...	44.3	...
Jones.....	50.0	43.8	43.8	41.7	39.6	52.1	45.9	...	...	...	...	40.0	...
McGill.....	46.1	40.0	46.1	...	...	...	...	...	44.9	51.1	...	52.4	...
Snell and Scott.....	37.3	45.7	46.8	38.1	48.4	33.3	46.8	...	46.0	...	44.4	42.9	39.7
PER CENT OF SAMPLES AT AND BELOW MEAN:													
Bryan.....	57.2	57.4	62.0	53.8	57.2	57.4	55.1	...	53.4	...	...	55.7	...
Jones.....	50.0	56.2	56.2	58.3	60.4	47.9	54.1	...	...	...	...	60.0	...
McGill.....	53.9	60.0	53.9	...	...	...	...	...	55.1	48.9	...	47.6	...
Snell and Scott.....	62.7	56.3	53.2	61.9	51.6	66.7	53.2	...	54.0	...	55.6	57.1	60.3

general, the syrups from the Lake Huron district (Simcoe, Grey and Bruce Counties) are high in total ash, conductivity, lead values and malic acid value. But the majority of the syrups from that district were made by rather primitive methods. Kettles

may be instrumental in raising these values in 36, 39, 95, 96 and (119).<sup>1</sup> A number of instances appear, also, in which high moisture content is *not* accompanied by high analytical values, *e. g.*, Nos. (45, 59), 61, (102), 115 (high in malic acid) and 125. Again,

<sup>1</sup> THIS JOURNAL, 5, 740.

<sup>1</sup> Serial numbers in parentheses refer to syrups not included in Table I.

No. 81, although made with a patent evaporator without a clarifying agent, evaporated to the correct water content (34.66 per cent), filtered through flannel and allowed to settle, is exceptionally high in total and insoluble ash, alkalinity of insoluble ash, Canadian and Winton lead values and malic acid value. This syrup came from a bush on lime soil, a fact that may have some connection with its composition. No. (104, 114) and 121, fairly high in the same values, are also from limestone soils, but we have instances, such as Nos. 3, (4), 100, (102, 108, 111 and 113), of syrups which come from limestone soils but are not high in these analytical values.

Among these syrups there are five—Nos. 33, 36, 39, 95 and 96—which show higher conductivity values than the maximum (200) reported in Paper I. The five are all from the adjacent counties of Simcoe and Grey, Ontario. Four of the five were kettle-boiled and treated with eggs or milk or both. No. 96 received 2 eggs and 4 cups of milk to 4 gallons of syrup; No. 95 was pan-boiled and not treated with eggs or milk. Four of the five contained excess of water, but No. 33, which had the highest conductivity value, was exactly right in water content. The collector

syrups range from 10.7 to 18.3 per cent of the value at 25°.

#### RANGE OF VARIATION OF THE ANALYTICAL VALUES

In Tables IV and V we have set forth the maximum, minimum and average results obtained in the analysis of genuine maple syrups in the four most extensive investigations that have been published. In Table IV, the range of variation of each value in the work of each investigator is expressed in percentage of the mean. Table V gives the average results and the extreme variations of the four investigations taken together, the range of variation being expressed both in percentage of the mean and in percentage of the minimum.

Some explanatory statements are necessary in reference to the data of Tables IV and V. Bryan's investigation covered 481 syrups, collected from all of the important maple-producing sections of the United States and from the Province of Quebec. The collection was made by disinterested officers, whose names are published in Dr. Bryan's bulletins. They were instructed to be present at the manufacture of the syrup, whenever practicable. The measures

TABLE V.—SUMMARY OF RESULTS OF ANALYSES OF GENUINE MAPLE SYRUPS. ALL ON MOISTURE-FREE BASIS  
Canadian lead No. Winton lead No.

	Total ash	Soluble ash	Insoluble ash	Soluble ash insoluble ash	Sol. ash	Alkalinity		5 g. syrup	5 g. dry matter B	Modified		Conductivity value
						Insol. ash	Alk. sol. ash Alk. insol. ash A			25 g. syrup A	25 g. dry matter B	
No. of analyses.....	770	770	770	655	655	655	655	456	126	528	126	1746
Average .....	0.96	0.59	0.37	1.74	0.74	1.00	0.80	2.83	3.48	2.62	2.30	148
Maximum .....	1.68(b)	1.23(b)	1.01(b)	3.86(b)	1.22(b)	2.08(b)	1.83(b)	6.56(m)	7.50(a)	4.41(b)	4.09(a)	230(a)
Minimum .....	0.61(a)	0.30(a)	0.12(m)	0.53(b)	0.41(b)	0.41(b)	0.21(b)	1.37(m)	1.74(a)	1.05(m)	1.41(a)	0.29(b)
Difference .....	1.07	0.93	0.89	3.33	0.81	1.67	1.62	5.19	5.76	3.36	2.68	131
Range in % of av.....	111	158	241	191	109	167	203	183	166	128	117	164
Range in % of min.....	175	310	742	628	198	407	771	379	331	320	190	452

(a) By authors. (b) By Bryan. (m) By McGill. (d) In a Vermont syrup. See Paper I.

(c) 194 actual samples, 22 of which are reckoned as 2 in averaging. See Paper I.

of Nos. 33, 36 and 39 wrote that "these samples were all collected from the bush where the syrup was made, so that there was no possibility of it being adulterated." The collector of Nos. 95 and 96 states that these samples also were collected from the bush and that they were "made for home use." While these results indicate the possibility of a genuine maple syrup showing a conductivity value of over 200, they also show that such a high conductivity is rare, and perhaps never occurs in a marketable syrup. The highest conductivity values found in those syrups of this collection which were made in modern evaporators are 192 and 177. The syrup that gave the former value had been treated with eggs and milk.

#### CONDUCTIVITY VALUES AT 20° C. AND 25° C.

We have determined the electrical conductivity at 20° C. of ten of the syrups showing high values and of ten showing low values at 25° C. The results are shown in Table III. The maximum at 20° is 202, the minimum 94. The minimum does not occur in the same syrup as at 25°. The average of the ten high values at 20° is 12.1 per cent less than at 25°, the average of the ten low values at 20° is 12.5 per cent less than at 25°. The differences in the individual

adopted to exclude adulterated samples from the collection appear, therefore, to have been practically identical with our own. Whether they were as successfully carried out we are, of course, not in position to judge. The variations shown in the results are, in general, much wider than those in any of the other investigations. But the territory covered was much wider and the number of samples analyzed greater than in any other instance.

The investigations of Jones embraced 48 syrups, presumably all Vermont syrups.

McGill's 456 syrups were sent in by the producers with a declaration of genuineness—a method of collection which perhaps affords less security against the inclusion of adulterated samples than that adopted by Bryan and ourselves. Like our own, McGill's samples were all from the Provinces of Ontario and Quebec. His Canadian lead number determinations were made upon all the 456 samples; malic acid determinations on 452; total, soluble and insoluble ash on 115; and Winton lead number on 47.

Bryan's "basic," *i. e.*, Winton, lead number was determined upon 25 grams of syrup and calculated to the basis of 100 grams dry matter. The figures given in our table for his average ratios of soluble



to insoluble ash and of alkalinity of soluble to alkalinity of insoluble ash are the true averages of the ratios of the individual syrups. The figures given for these averages in this publication are evidently derived by dividing the average soluble ash by the average insoluble ash, and the average alkalinity of soluble by the average alkalinity of insoluble ash. This involves the assumption that the ratio of the averages of two sets of numbers is equal to the average of the ratios of the individual numbers—a proposition that is not mathematically true. Thus, instead of the figure 1.70 given in his summary for the average ratio of soluble to insoluble ash the correct average is 1.84, and instead of 0.77 for the average ratio of the alkalinities the correct figure is 0.81. Of the two kinds of malic acid value determined by him that given in our tables is the one determined by the A. O. A. C. method.

Jones has made the same error as Bryan in calculating the average ratio of soluble to insoluble ash. We have used the true average, 1.78. The ratio of the alkalinities ascribed to him has been calculated from his results. His tables give the ratios of the alkalinities of one gram soluble to that of one gram insoluble ash, but not the ratios of the actual alkalinities of the two portions of the ash.

McGill's Winton lead numbers, like Bryan's, were determined with the use of 25 grams syrup and calculated over to the basis of 100 grams dry matter, notwithstanding the fact that, consequent upon his investigation, a modified method (using instead of 25 grams of syrup, the quantity of syrup containing 25 grams of *dry matter*) was adopted for the official Canadian standard of purity. The Canadian lead number also was determined on 5 grams of syrup but calculated over to the basis of 100 grams dry matter—which again is not the method adopted as the official standard.<sup>1</sup> It seems probable that the malic acid value was likewise determined upon 6.7 grams of syrup and calculated to the basis of 6.7 grams dry matter, although here again the use of the quantity of syrup containing 6.7 grams of dry matter is prescribed in the standards based upon the work.

As already noted, our own results upon Canadian lead value, Winton lead value and malic acid value were obtained with the use of the quantities of the syrups which contained 5, 25 and 6.7 grams of *dry matter*, respectively. Our lead values are, therefore, not strictly comparable with any of the others, and it is doubtful also whether our malic acid values are fairly comparable with the others. Since, however, our malic acid values all fall within the limits reached in the work of the other investigators, this latter point is not of consequence. We have designated our Winton numbers "modified" and placed them in a separate column to call attention to the difference of method. To be quite consistent we ought to have done the same with the Canadian lead number.

In Table V, the averages have been calculated from

the averages of the four investigations included in Table IV. The minimum conductivity value given in Table IV is that found in the syrups whose analysis is here reported. That given in Table V is the minimum found in our whole experience with genuine syrups (194 samples).

#### COMPARISON OF THE VARIOUS ANALYTICAL DATA

Tables IV and V appear to throw much light upon the relative merits of the various analytical data as means of detecting adulteration in maple syrup. The total ash, the soluble ash, and especially the alkalinity of the soluble ash are shown to be of relatively narrow range and, therefore, much more useful than the insoluble ash or its alkalinity. In view of the not infrequent use of soda as a clarifying agent, the narrowness of range of the alkalinity of the soluble ash is a thing that would scarcely have been foreseen.

The amount of insoluble ash shows the widest variation of all the values, not only among the investigations taken as a whole but also among the results of each individual investigator. Considering the opportunities which maple syrup has to become contaminated with clay and iron rust, this is perhaps not surprising. Considered with respect to its minimum, the amount of insoluble ash has been regarded as an important datum in the detection of adulteration in maple products. Jones found no samples below 0.25, and Bryan none below 0.23 per cent in insoluble ash. McGill, however, finds 12 out of 115 samples below 0.23 and his minimum value is 0.12—just one-half the minimum found by the two investigators in the United States. It was partly this striking divergence that induced us to undertake the present investigation. The outcome has been to confirm, at any rate to a certain extent, McGill's conclusion that the insoluble ash in Canadian syrups is not infrequently below the minimum found by Bryan. Our minimum is 0.16 and 4 samples out of 126 fall below 0.23. These low results can not have been due to overheating in the ignition. Our ash determinations were made in an electric muffle at a temperature never exceeding 650° C., as indicated by a Hoskins pyrometer. The determinations on the four samples in question were made in duplicate. In our experience treating the ash with ammonium carbonate and reheating produces no increase in weight, showing that no loss of carbon dioxide occurs under the conditions of our ash determinations. Results as low, or nearly as low, as our minimum (0.16 per cent) are, however, extremely rare. McGill has only two results, and we only two, below 0.19—a total of only 4 below 0.19 in the 770 analyses of the four investigations.

The alkalinity of the insoluble ash, although less variable than the weight, is far from being of equal value with the total or with the soluble ash figures. The ratios of soluble to insoluble ash and of alkalinity of soluble to insoluble ash are so widely variable as to appear to us scarcely worth reckoning. The malic acid value is about as variable as the alkalinity of the insoluble ash. The minimum for this value is much lower than the work of Jones indicated.

<sup>1</sup> In Paper II, we have shown that direct determination of these two lead numbers upon a quantity of syrup containing a definite quantity of dry matter gives results which do not coincide with those calculated to dry matter from a fixed quantity of syrup. THIS JOURNAL, 5, 1913, 997.

The Winton lead value makes a good showing on the dry basis and, as will be shown later, a much better showing on the wet basis. The Canadian lead method yields a value of comparatively wide range, but, as we have already shown, this method has a very important advantage over all the others in another respect.

In the general comparison (Table V) the conductivity value shows the narrowest range of all the values. In view of the relatively small number of samples upon which this determination has been made we hesitate to advance too positive claims on its behalf: judging

state of affairs (see Table VI). The range of variation on the wet basis is 71 per cent of the average as against 76 per cent of the average on the dry basis; or 119 per cent of the minimum, as against 127 per cent.

Taking Bryan's and McGill's results together (as in Table V) we find the average Winton lead value, on the wet basis (528 samples) to be 1.73. The maximum (Bryan) is 2.70, the minimum (McGill) 0.70. Difference 2.00. Range in percentage of average 116, as against 128 for the dry basis value. Range in percentage of minimum 286, as against 320 for the dry basis value. It would appear, therefore, that the

TABLE VI—COMPARISON OF WINTON LEAD NUMBER ON DRY AND ON WET BASIS

BRYAN'S SAMPLES				MCGILL'S SAMPLES					
		Winton lead value				Winton lead value			
Sample	County and State	Moisture content			Sample	Maker	Moisture content		
			Dry basis	Wet basis				Dry basis	Wet basis
HIGHEST VALUES									
6401	Champaign, O.	46.71	4.41	2.35	iii	J. Jacques, Burgessville, Ont. (a)	33.82	2.31	1.53
6842	Somerset, Pa.	36.96	4.28	2.70	iv	J. C. Skinner, Burgessville, Ont.	35.68	2.36	1.52
6301	Logan, O.	38.63	4.24	2.60	v	H. A. Griswold, Burgessville, Ont.	35.08	2.29	1.49
6654	Upshur, W. Va.	35.81	4.20	2.70	xvi	J. E. Rice, New Durham, Ont.	35.22	2.30	1.49
6399	Madison, Ind.	39.04	4.05	2.47	xviii	E. T. Chambersy, Oxford Centre, Ont.	28.14	2.08	1.49
6278	Logan, O.	38.17	4.01	2.48	xxi	M. Sager, Vandicar, Ont.	33.62	2.25	1.49
6984	Mahoning, O.	30.09	3.86	2.70	i	G. H. Losee, Burgessville, Ont.	38.32	2.38	1.47
LOWEST VALUES									
6693	Oxford, Me.	33.23	1.76	1.18	11	W. H. McAllister, Dutton, Ont.	34.94	1.08	0.70
6635	Rutland, Vt.	37.70	1.85	1.15	207	Wilfrid Larose, Angers, Que.	36.56	1.12	0.71
					392	J. F. Parsons, Barnston, Que.	34.07	1.07	0.71
					176	J. Y. Williams, Wisbeach, Ont.	31.12	1.05	0.72
Average 481 samples		34.22	2.70	1.78	Average 47 samples		34.61	1.75	1.17
Maximum			4.41	2.70	Maximum			2.38	1.53
Minimum			1.76	1.15	Minimum			1.05	0.70
Difference			2.65	1.55	Difference			1.33	0.83
Range in percentage of average			98.0	87.0	Range in percentage of average			76.0	71.0
Range in percentage of minimum			151.0	135.0	Range in percentage of minimum			127.0	119.0

(a) Erroneously given as Quebec in McGill's bulletin. Burgessville is in Oxford County, Ontario.

from our results, this method not only excels all others in rapidity and ease of execution but is equal to any in respect to the narrowness of range of the value in genuine syrups and but little inferior to any, except the Canadian lead method, in the rate at which the value falls off with progressive adulteration of the syrup with sucrose.

In regard to the Winton lead number a point of curious interest is that the range of variation is narrower when the figures are referred to a definite weight of syrup than when they are reduced to the dry basis. The sample in Bryan's collection which gave the maximum "basic lead number" (No. 6401, Champaign Co., Ohio) was one abnormally high in water content (46.71 per cent). The dry basis value, 4.41, for such a syrup is equivalent to 2.35 per 100 grams syrup. A number of other syrups in Bryan's collection give higher values than 2.35 on the wet basis. (See Table VI.) The highest value on the wet basis is 2.70. This is given by three samples. Similarly, the sample which gives the lowest value on the wet basis is not identical with that which gave the lowest on the dry basis. The minimum on the wet basis is 1.15. The range of variation on the wet basis amounts to only 87 per cent instead of 98 per cent, expressed in terms of the mean; or to 135 per cent, instead of 151 per cent, expressed in terms of the minimum.

Turning to McGill's samples, we find the same

reduction of Winton lead values to the dry basis is labor misspent.

For the Canadian lead value, however, the same does not hold true. Taking McGill's results, determined on the wet basis and calculated over to the dry, we find:

TABLE VII—CANADIAN LEAD VALUE

	Wet basis	Dry basis
Average	1.91	2.83(a)
Maximum	4.68	6.56
Minimum	0.89	1.37
Difference	3.79	5.19
Range per cent of average	198.0	183.0
Range per cent of minimum	426.0	379.0

(a) We find McGill's average for moisture content to be 32.58. His moisture determinations were made by drying on asbestos fiber.

Here the dry basis has decidedly the advantage. In our own work, where the method prescribed by the Canadian standards was followed, the limits are still narrower (see Table V). But as our work embraced a much smaller number of samples than McGill's, we are not in position to decide whether the method followed by McGill (determination on 5 grams syrup and calculation to 100 grams dry matter) or that adopted for the standard (determination on the quantity of syrup containing 5 grams dry matter and multiplication by 20) is preferable.

## DISTRIBUTION OF RESULTS ABOUT THE MEAN

The lower half of Table IV shows that the general tendency of the analytical values is to run below, rather than above, the mean. Comparing each investigator's results on each value, we find only 5 cases out of 34 in which the deviation of the minimum from the mean is equal to, or greater than, that of the maximum. Two of these—the ratio of soluble to insoluble ash and the alkalinity of the insoluble ash—occur in Jones' work; the other three—per cent soluble, Winton lead number and malic acid value—occur in McGill's. In regard to the number of samples falling each side of the mean we find only 3 cases out of 34 in which the number above the mean is equal to, or greater than, the number below the mean. These are Jones' alkalinity of insoluble ash and McGill's Winton lead value and malic acid values. In all three of these cases very little over half the samples are above the mean.

## A SCHEME OF RAPID ANALYSIS

In the light of the preceding we venture to propose the following scheme of analysis (Table VIII), not as all-sufficient for detection of adulteration of maple syrup, but as a rapid scheme that will serve to condemn many samples and thus obviate the making of other determinations, involving additional time and labor:

TABLE VIII SCHEME FOR RAPID ANALYSIS OF MAPLE SYRUP

DETERMINATION	TIME REQUIRED		LIMITS OF VALUE	
	Actual attention	To reach result	Extreme	Ordinary
Refractometer reading....	5 min.	5 min.	.....	.....
Conductivity value 25° C.	5 min.	5 min.	110-230	113-205
Total ash, dry basis.....	7 min.	1½ hrs.	0.61-1.68	0.69-1.47
Alkalinity of soluble ash, dry basis.....	5 min.	½ hr.	41-122	48-109
Canadian lead number, 5 g. syrup, dry basis.....	12 min.	5 hrs.	1.37-6.56	1.51-4.55
Winton lead number, 25 g. syrup, wet basis.....	17 min.	9 hrs.	0.70-2.70	0.76-2.47
Total time required.....	51 min.	9 hrs.		

In Paper I it was shown that the conductivity test alone served to condemn 15 samples out of a collection of 34, purchased in the Canadian West, while the additional determinations made (*viz.*, total ash, insoluble ash, alkalinities of soluble and insoluble ash and modified Winton lead number) detected only two additional cases of adulteration. Of these two both would be condemned by the total ash and one by the Winton lead number. We believe the six determinations here recommended will in many instances prove equally as serviceable in the detection of adulteration as the twelve made by us on the syrups of Table I.

The extreme limits given for the values are the highest and lowest found in any of the syrups included in Table V. Under Canadian lead number, dry basis, we have included only McGill's results and the limits given are for determination upon 5 grams syrup and calculation to dry basis. Under Winton lead number, wet basis, we have included McGill's and Bryan's results. The limits for each investigator's work singly are much narrower (see Table VI). As ordinary limits of the values we have chosen the values not ex-

ceeded in either direction by more than one per cent of the samples analyzed. Thus, in the case of the total ash (770 samples) there are not more than eight samples below 0.69 and not more than eight above 1.47. Our time estimate is in each instance the minimum required for a single determination. In some cases it might be reduced by carrying on a number of determinations simultaneously. The 9 hours assigned to the Winton lead number determination provides for 4 hours settling of the lead sulfate precipitate. All six of the determinations can be made within these nine hours.

## SUMMARY

I. The results of the analysis of 126 samples of genuine Canadian maple syrup are reported.

II. The range of conductivity value for 20° C. in these syrups is determined, as well as that for 25°.

III. The range of the various analytical values in genuine maple syrups is compared with reference to these results and to those of Bryan, Jones and McGill.

IV. The values of narrowest range are the conductivity value, the alkalinity of the soluble ash, the weight of the total ash and the Winton lead number.

V. A scheme of rapid analysis is proposed, embracing determinations of the aforesaid values and of the Canadian lead number.

The expenses of this investigation were defrayed out of the Dominion Grant for the encouragement of Agriculture, 1912.

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## THE EFFECTS OF THE ENSILAGE PROCESS ON THE SOLUBILITY OF FLOATS

By E. B. FORBES AND CHAS. M. FRITZ

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One of the standard methods of adding floats to the soil is through its addition to manure, and the effect of the fermentation of manure on the solubility of floats has been the subject of discussion and experiment.

It has occurred to the writers that perhaps we might profitably add a part of the floats to the plant-food two steps further from the soil by introducing it into the silo with the fodder corn, thus gaining two opportunities for increasing the solubility of the floats, first in the ensilage process, and second in the digestive tract of the animal; and further, giving to the animal such benefit as it might be able to get from the rock phosphate in its passage through the body. We do not mean to suggest, however, that all of the floats which one might desire to add to the soil could in this way be passed through the silo and the animal.

In this test four samples of corn were prepared as follows:

1. Untreated green silage corn.
2. Silage from No. 1.
3. Green silage corn plus floats (250:1).
4. Silage from No. 3.

The silage was made in glazed earthen jars. After being sealed for 6 months the jars were opened, and the silage was found to be in perfect condition.



At the time the treated corn was sealed up the floats gave it a sandy feeling between the teeth, but in the silage from this corn the "grit" had disappeared. We were able to detect no difference in the taste, odor or appearance of the two samples of silage.

The following phosphorus estimations were made on these two samples of silage and on the fresh materials from which they were prepared.

PHOSPHORUS IN SILAGE CORN WITH AND WITHOUT ADDED FLOATS, AND IN SILAGE MADE FROM THE SAME. PER CENT, WATER-FREE BASIS

Product	Total P	Water-sol. P	Citrate-sol. P	Inorganic P sol in 0.2% HCl	Total water-sol + citrate-sol. P
Untreated green silage corn..	0.200	0.151	0.020	0.086	..
	0.203	0.150	0.021	0.082	..
	0.218	0.147	0.021	0.082	..
Average.....	0.207	0.149	0.021	0.083	0.170
Silage from untreated corn..	0.231	0.159	0.009	0.112	..
	0.228	0.161	0.007	0.110	..
	0.214	0.161	0.009	0.112	..
Average.....	0.224	0.160	0.008	0.111	0.168
Green silage corn plus floats (250 : 1).....	0.374	0.135	0.055	0.156	..
	0.371	0.138	0.064	0.181	..
	0.367	0.135	0.065	0.178	..
Average.....	0.371	0.136	0.061	0.172	0.197
Silage from treated corn....	0.405	0.158	0.061	0.234	..
	0.387	0.157	0.061	0.243	..
	0.361	0.155	0.059	0.235	..
Average.....	0.384	0.157	0.060	0.237	0.217

The increase in total phosphorus during the ensilage process shows that there was a loss of 8.2 per cent of dry substance from the untreated corn and 3.5 per cent from the phosphated corn.

The increase in water-soluble phosphorus in the untreated corn was not quite equal (7.4 per cent) to the arithmetical increase due to the loss of dry matter.

During the ensilage of this untreated corn there was a loss of citrate-soluble phosphorus, in the residue from water extraction, which signifies a process of reversion to less soluble forms.

The one significant increase during the ensilage of the untreated corn was in the inorganic phosphorus soluble in 0.2 per cent HCl. This was much more than enough to account for arithmetical increase from loss of dry substance.

In the phosphated corn there was a loss of water-soluble phosphorus simply through the addition of the floats, that is, the water-soluble phosphorus in the fresh corn was 0.149 per cent and in the phosphated corn 0.136 per cent, which probably signifies a combination of water-soluble phosphorus of the corn with bases in the floats. This probably took place during the partial drying at 50° C., though perhaps to some extent during the subsequent storage of the sample for nearly a year before the analyses were made.

The water-soluble phosphorus in the phosphated silage was not higher than in the untreated silage. The excess of water-soluble phosphorus in the phosphated silage over the amount in the unsiled, phosphated corn was more than enough to account for the loss in dry matter, but was not as great in amount as in the silage from the untreated corn, again suggesting reversion.

The citrate-soluble phosphorus in the treated fodder and in the silage from the same was naturally higher than in the untreated corn and silage, since a part of the phosphorus of the floats was citrate-soluble. There was no increase in citrate-soluble phosphorus, however, in the residue from the water extraction, during the ensilage of the phosphated corn.

The very considerable increase in inorganic phosphorus soluble in 0.2 per cent HCl during the ensilage of the phosphated corn gives us the most significant figure of the test. In the treated corn fodder the inorganic phosphorus soluble in 0.2 per cent HCl was 46.4 per cent of the total, while in the silage from the same was 61.7 per cent of the total.

It is also of interest that the phosphated silage contained more than twice as much inorganic phosphorus soluble in 0.2 per cent HCl as the treated silage.

The total phosphorus of the floats was 12.666 per cent, the water-soluble phosphorus 0.0129 per cent and the phosphorus soluble in 0.2 per cent HCl 8.721 per cent, all on a water-free basis.

CONCLUSION—The ensilage of corn will render soluble in 0.2 per cent HCl such an amount of the phosphorus of floats, added to corn, as to constitute a practical consideration in the feeding of livestock.

DEPARTMENT OF NUTRITION  
OHIO AGRICULTURAL EXPERIMENT STATION  
WOOSTER

## THE EFFECT OF HEAT UPON THE SOLUBILITY OF THE MINERAL CONSTITUENTS OF THE SOIL<sup>1</sup>

By WILLIAM MCGEORGE<sup>2</sup>

Received November 5, 1913

Heating soils as a means of stimulating growth of crops is a practice established centuries ago, but owing to the difficulties encountered in its application it has not been extensively used in practical agriculture, and consequently has gradually fallen out of use. Those who have investigated the cause of this stimulation have, as was to be expected from the extremely complex nature of soils, differed in their results and conclusions. It is certain, however, that the phenomenon is not explainable by any one theory, but the action is dependent upon the chemical, biological, and physical properties of the soil.

In Hawaii certain crops are greatly influenced, both in color and vigor, by the mere burning of brush and undergrowths of guava and lantana upon the surface. In tropical soils, which receive practically no "rest," it is probable that the effects of heat are similar to those derived from cultivation and aeration. With but few exceptions it is found necessary in Hawaii to plow the new land and follow with thorough tillage at frequent intervals for several months before planting. On the other hand the same results may be accomplished by means of heat.

Investigators have studied this question from various standpoints, among these being the effect of the heat upon the solubility of the mineral constituents. However, the majority have confined their studies to phosphoric acid; several have included potash and nitrogen,

<sup>1</sup> Published by permission of the Secretary of Agriculture.

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while but comparatively few have gone beyond this and determined the effect upon the remaining soil constituents. The object of the work, here presented, was to add to the information regarding the effect of heat upon all the common mineral constituents of the soil. Distilled water and fifth-normal nitric acid were used as solvents.

Probably the most valuable work on the solubility of the mineral constituents of soils is to be found among the publications of the U. S. Bureau of Soils, their work being largely confined to the use of water as solvent. In a bulletin of this Bureau<sup>1</sup> King gives comparative results of work upon fresh and oven-dried soils which show the effect of heating to  $110^{\circ}\text{C}$ . to be quite striking. On the average, more nitrates, phosphoric acid, sulfuric acid, carbonic acid, and silica were recovered from the oven-dried than from the air-dried soil, while the average of the chlorine determinations showed a decrease. No determinations of basic constituents are given, but it is stated that upon later investigation an increase was found in the solubility of potash, lime, and magnesia in oven-dried soils.

**METHOD OF PREPARING EXTRACTS**—Extracts were made upon the soils in proportions of 1 part soil to 5 of water or fifth-normal nitric acid. The conditions of the samples treated were air dry, heated to  $100^{\circ}\text{C}$ . for eight hours, heated to  $250^{\circ}\text{C}$ . for the same time and over the full flame of the Bunsen burner (in porcelain dishes). The latter were heated carefully at first to prevent dusting and finally for two hours over the full flame. Water extracts were obtained by shaking for one hour and allowing to settle twenty-four hours and then filtering. Nitric acid extractions were made by shaking for 5 hours and then filtering directly.

**TYPES OF SOIL**—In choosing the soils to be used in this work a series of twelve soils were chosen, which included in a general way the normal and abnormal types, both physical and chemical, occurring on the islands. These include both red and yellow heavy clays, sandy and silty soils, highly manganiferous (9.74 per cent  $\text{Mn}_2\text{O}_3$ ), highly titaniferous (20 per cent  $\text{TiO}_2$ ) soils, a soil containing 8.7 per cent  $\text{MgO}$ , submerged soils both in the wet and subsequently air-dried states, and finally soils both high and low in organic matter.

In this paper only the results will be discussed. The complete analytical data and a more comprehensive discussion will be found in a bulletin of the Hawaiian Experiment Station.<sup>2</sup>

The elements determined were silica, alumina, iron, manganese, lime, magnesia, potash, sulfates, phosphoric acid and bicarbonates. The results obtained upon the solubility of the first three of these substances in water are rather inconsistent. This is probably due to the slight solubility of these elements toward this solvent. On an average the solubility of alumina and silica increased with increase in temperature up to ignition. Iron was most soluble in the air-dry sample. This latter fact is in direct harmony with former experiences, namely, that under normal conditions in Hawaii, part of the iron exists in the form of

ferrous compounds. Hawaiian soils, while characteristically basic, normally give an acid reaction, due indirectly to the high clay content and its accompanying poor aeration. Further confirmation of this fact is to be found in a comparison of cultivated and uncultivated soils, in which the iron content of the latter is more soluble. Also, the solubility of iron in rice and taro soils, in the submerged state, is strikingly high, and is greatly decreased as a result of heat and its accompanying oxidation. The data obtained by using  $N/5$  nitric acid as solvent disclose some very interesting facts, and give almost conclusive proof of an increase in solubility of these three constituents as effected by heat. The results indicate a gradual increase with increase in temperature up to ignition.

These effects on the solubility, especially in water, are probably referable to a number of causes. It is primarily physical, being related to an alteration of the films surrounding the soil particles and to a modification of the colloidal forms which these elements probably assume under the prevailing conditions. Dehydration and certain chemical alterations at the higher temperatures would also tend towards increasing the solubility in acids through the action of heat upon the hydrated silicates. It has long been known that certain hydrated silicates of aluminum become more soluble in acids as a direct effect of heat. The ancient art of alum manufacture took advantage of this fact. The samples highest in magnesia content show the greatest solubility of silica in  $N/5$  nitric acid. The alumina was found to be most soluble in the highly organic soils and in addition proved to be considerably more soluble than the iron in every sample.

**MANGANESE**—The solubility of manganese in water was greatest in the samples ignited, if it be permissible to draw conclusions from an average. However, the data were somewhat inconsistent and not in harmony with field conditions as induced by cultivation; that is, an analysis of the same soil cultivated and uncultivated showed a decrease in solubility as a result of aeration. Apparently the effect of heat upon the manganese is partly chemical as well as physical.

The solubility of  $N/5$  nitric acid as affected by heat shows a remarkably consistent increase in solubility up to  $250^{\circ}\text{C}$ ., followed by a large decrease in the ignited samples. This is true with only two exceptions in the entire series. This element occurs in some Hawaiian soils in the form of concretions and hence is present, at least partially so, as manganese dioxide. But in the normal soils these are absent and here the manganese exists in a lower state of oxidation and hence in a more soluble form. In each instance manganites or other salts may occur to a limited extent. With one exception the oxides of manganese are quite insoluble in nitric acid, this oxide being manganous oxide ( $\text{MnO}$ ). Therefore the solubility of the oxides would increase with increase in temperature, owing to a decrease in state of oxidation,  $\text{MnO}_2$  being converted into  $\text{Mn}_2\text{O}_3$  and  $\text{Mn}_3\text{O}_4$ , each of which are partially soluble in nitric acid for the reason that they are combinations of the oxides  $\text{MnO}$  and  $\text{MnO}_2$ . Since  $\text{Mn}_3\text{O}_4$  contains the largest amount of  $\text{MnO}$  it is

<sup>1</sup> U. S. Dept. Agr., Bur. Plant Indus., *Bull.* 26.

<sup>2</sup> Hawaii Agr. Expt. Sta., *Bull.* 30.

evident that at this temperature greater solubility in  $N/5$   $HNO_3$  would result, due to the formation of this oxide. In addition to the above facts it is known that the action of heat on organic compounds of manganese, as well as other of its salts, is to convert them into oxides.

**LIME AND MAGNESIA**—From a study of the data obtained from the determinations of these two elements it was found that they were both most soluble in water in the samples heated to  $250^\circ C.$ , increasing with increase in temperature up to  $250^\circ C.$ , and decreasing again upon ignition. In nitric acid the lime is most soluble in the samples heated to  $100^\circ C.$ , and least soluble in the ignited samples. The general tendency is for the magnesia to be affected in a similar way. Thus we are led to conclude that the action of weak nitric acid in no way correlates with that of distilled water. The highly organic soils proved to hold the lime in the more soluble form. It is also worthy of note that the effect of cultivation was to cause an increase in the solubility of these elements. Another important fact brought out was that even though most of the soils used in this series show, from digestion with  $HCl$  (sp. gr. 1.115), a higher magnesia content than lime, one four times as much, yet the lime with few exceptions is present in higher concentration in the extract.

The effect of heat upon the solubility of these two elements is more striking than are the results obtained from the remaining elements. It is highly probable that the increased concentration of the water extract of the sample heated to  $100^\circ C$  over the air-dried samples is the result of physical causes, namely destruction of the soil film and dehydration accompanied by a slight decomposition of organic matter. On the other hand the samples heated to  $250^\circ C.$  undergo all the above transformations more completely and in addition suffer a more complete decomposition of organic matter. Since calcium and magnesium are two elements universally combined with organic matter in the soil there necessarily follows an increase in solubility as a result of the more complete decomposition. The soils containing the highest per cent of organic matter contained these two elements in the most soluble form.

The decrease in solubility of lime and magnesia in water upon the ignited samples and in nitric acid at  $250^\circ C.$  and ignition is hard to explain. It is undoubtedly partly due to chemical changes in the soluble forms resulting from the decomposition of the organic matter, also in the decrease in exposed surfaces as a result of the aggregation of the soil particles and other physical factors. It is suggested that one of the chemical changes taking place is that of a replacement of the potash and soda in the silicates by magnesium and calcium, as a direct result of heating. The data obtained in this work show a decided decrease in solubility of lime and an increase in that of potash upon ignition in a majority of the samples. In addition to the above-mentioned factors a decrease in solubility at ignition would be produced by the conversion of the bicarbonates into normal carbonates, the latter being less

soluble. This would, of course, be more noticeable in the water extracts.

**POTASH**—The soils heated to  $250^\circ C.$  and ignition yield the more concentrated solution of potash, the average being in favor of the ignited soils. It was found that the solubility of the potash was increased by cultivation, and that in the highly organic soil to be the most soluble. The general ideas involved in the effect of heat will be dealt with more thoroughly in the discussion to follow, and for this reason the solubility of the potash requires little comment at this point. The fixing of potash is generally held to be due to hydrated silicates and organic matter. Cameron and Bell<sup>1</sup> on continuously extracting a soil with water until no more potash dissolved, then grinding the sample and re-extracting, found an additional amount of potash to be removed. This they attributed to a colloidal aluminum silicate upon the surface of the particles, thus protecting them from the action of the water as well as absorbing the potash. Dehydration and decomposition would therefore materially overcome the fixing power and the potash subsequently replaced by lime or magnesia would not become refixed during a short period, and heat would also liberate more potash from the insoluble form.

**PHOSPHORIC ACID**—The solubility of this constituent as affected by heat indicates a minimum in the air-dry soils and the maximum in those heated to  $100^\circ C.$  and  $250^\circ C.$  It is worthy of note that phosphoric acid is more soluble in the uncultivated than the cultivated soils, and that the former decreases in solubility with increase in heat. The nitric acid extracts show a gradual increase in solubility with increase in heat, being most soluble in the ignited samples.

Phosphoric acid exists in soils in the major part combined with iron, aluminum, magnesium, calcium and organic matter. It may be in the form of basic phosphates, hydrogen phosphates, or as double phosphates in combination with more than one element. It is probably combined mostly with iron, aluminum and titanium in Hawaiian soils. Considerable work has been done upon the effect of heat upon the solubility of this constituent and attempts have been made to draw conclusions from these results as to its state of combination, that is whether organically or inorganically combined. Peterson<sup>2</sup> using  $N/5$  nitric acid found that after oxidizing the organic matter with hydrogen peroxide there was no increase in solubility when the soil was subsequently heated to  $240^\circ C.$  He concluded, therefore, that the solubility of the mineral phosphates in soils is not increased up to  $240^\circ C.$  The results obtained from the water extracts of Hawaiian soils indicate a decrease in solubility at high temperatures due either to a chemical change to a form less soluble in water or an increase in absorbing power of the soil. The increase at  $100^\circ$  and  $250^\circ$  is undoubtedly partly due to a destruction of organic matter and to a breaking up of the colloidal film. The action of dilute nitric acid is somewhat different in that an increase in solubility upon ignition results, accompanied by that of iron, aluminum, silica and titanium. Iron and alumina

<sup>1</sup> U. S. Dept. Agr., Bur. Soils, Bull. 30, p. 26.

<sup>2</sup> Wis. Exp. Sta., Research Bull. No. 19.



occur, in Hawaiian soils, to a certain extent as hydrates or hydrated silicates, and, of course, would be more or less mechanically impregnated with phosphoric acid, as well as chemically combined. The effect of heat would directly increase the solubility of these constituents in nitric acid up to ignition, at which point the decomposition of the hydrates would be at a maximum while their colloidal properties would be practically nil.

**SULFATES**—Heat has a very striking effect upon the solubility of sulfates, most marked in the water extracts. In this series the air-dried soils were the least soluble, those heated to 100° C. next, while the maximum was reached in those samples heated to 250° C., finally decreasing upon ignition. On the other hand the ignited samples gave the most concentrated solution with nitric acid. One surprising feature of this series is that in many instances the sulfates were more soluble in water than in nitric acid, which is probably due to precipitation subsequent to extraction in the latter.

In connection with the solubility of the sulfates it should be mentioned that part of the increase in solubility of sulfates as a result of heat is probably due to absorption of the products of combustion of the gas used in heating the soils. King,<sup>1</sup> however, found an enormous increase in the solubility of sulfates upon heating in an oven at 110° C., using both gasoline and kerosene, thus eliminating this factor. In addition to the destruction of organic matter, soil films, etc., it is necessary to take into consideration the effect of heat upon the various inorganic sulfur compounds. Calcium sulfate is known to exist in four forms, two being anhydrous, one more soluble than the other. Sulfur also exists in soils as sulfides, generally with iron or as sulfate in combination with iron, lime or magnesia, as well as many essential forms of organic compounds. The effect of heat would be most marked upon the organic compounds in that they would be oxidized at the higher temperature, to the dioxide or trioxide which upon treatment with water as solvent would tend to form sulfuric acid or sulfates to the extent of the soluble bases present. On ignition it is evident that sulfur, especially that organically combined, would be volatilized upon ignition. An illustration of this action is well illustrated in the soil containing the highest amount of organic matter in the series. In this sample the increase of the sample heated to 100° C. over the dry-air sample was 1600 parts per million, while in passing from 250° C. to ignition the decrease amounted to 1900 parts per million.

**BICARBONATES**—The results of this series indicate a slight increase in solubility at 100° C. and 250° C., followed by a decrease upon ignition. Thus it appears that heat increases the amount of bicarbonates in the soil and at the same time increases the solubility of the bases. The decrease upon ignition is probably due to the transformation of the bicarbonates into normal carbonates, thus temporarily reducing their solubility in water.

**DISCUSSION**—The foregoing results show that an increase in solubility of the mineral constituents of

Hawaiian soils is effected by heating. It was to be expected that the results would be inconsistent, to some extent, because of the varying types of soil used. The samples represent most of the normal and abnormal types of the islands. That there are both chemical and physical factors concerned in the phenomena at hand must be admitted at the outset. However, the most important set of factors affecting the solubility of inorganic soil constituents appears to be of a physical nature.

Undoubtedly the means by which the physical factors act is through the soil moisture in its relation to the physical properties of the soil. The conditions conducive to the formation of a colloidal state and the subsequent relation of heat to the destruction of colloid are two of the most important of these factors.

It is certain that soil moisture distributes itself around the soil particles and in some instances as an impregnation within the particles. The moisture, therefore, occurs as thin films which, according to certain physical conceptions, must be held around the particle by an enormous pressure. From purely physical considerations this pressure has been estimated at several thousand atmospheres. Under such pressure the concentration of film water with reference to the mineral matter should be much greater than that of the free or capillary water in the soil.

Then the air-dried soil, the particles of which are still surrounded by a film of moisture, when shaken with water, should theoretically show the least solubility. Our results in most instances are in harmony with this assumption. But if the soil be allowed to remain in the condition and environment prevailing in submerged cultures, that is, in the presence of a large excess of water, then in time diffusion would bring about a more or less equal distribution of dissolved materials throughout the entire water present, and, therefore, the pressure of soil films would be decreased to a minimum or entirely eliminated. Hence the amount of materials going into solution in the free water present from such soils would be expected to be abnormally high. Upon air drying such soils the normal films would again appear with a resulting decrease in solubility. Subsequent heating ought then to affect these soils in a way very similar to that produced on dry land soils. The data obtained in the examination of rice soils is in harmony with this view.

Water, however, not only exercises a solvent action on minerals, but forms various hydrates, the solubility and physical character of which in some instances are greatly altered; organic as well as inorganic matter goes into solution with the result that the moisture films around the particles become solution films, holding in suspension and more or less intermingled with colloids, both organic and inorganic. The films then may be looked upon as being of a colloidal nature.<sup>1</sup>

Upon heating the soil to 100° C. alterations in the films would take place through evaporation and by partial dehydration of colloids thus destroying the pressure by which the film was previously held around the particles. At the temperature of 100° C. the con-

<sup>1</sup> No claim is made for originality in this view. The idea of soil films, colloidal films, jels, etc., has been made use of by various writers on soils.

<sup>1</sup> U. S. Dept. Agr., Bur. Soils. Bull. 26, p. 56

centration of the soil moisture would also be temporarily increased, due to increase in solubility with heat. During the course of the evaporation the concentration of the soil moisture would increase to the saturation point, after which the mineral matter would be deposited on the surface of the film as evaporation went on.<sup>1</sup>

Also the materials held in solution in the interior of the permeable particles would be partially deposited on the surface as the water evaporated. Upon adding water to the soil after having been dried, it is probable the materials deposited from previous evaporation would be more soluble than the other mineral constituents. In addition a certain amount of oxidation and other chemical changes in the organic matter might reasonably be expected to take place, which would have some effect on the solubility of the mineral bases that tend to combine with the organic matter.

Upon shaking with water a soil previously dried, the solution then obtained should be of a greater concentration than that prepared from the air-dried soil. With the absence of soil films and a more or less altered condition of the colloids present the solvent would have more ready access to the soil particles during a short period in addition to coming into immediate contact with salts deposited on the surface of the particles. In the light of these views then the solubility of soils before and after drying becomes more intelligible.

Why several of the mineral constituents of the soil should be so markedly more soluble when heated to 250° C. than at the other temperatures is a question not easily answered. The difference in physical effects were quite noticeable in that there was a greater aggregation of particles. Again there was a more complete destruction of organic matter effected at this temperature and also it is not entirely impossible that drying at 100° C. for eight hours does not effect a complete elimination of the soil moisture and especially the water of chemical combination. It seems reasonable then that the effects of heating to 100° C. are simply magnified when heated to 250° C. added to this being a more complete destruction of organic matter, the results both physical and chemical being of the same general nature but more complete at the higher temperature. The destruction of organic constituents being more complete would necessarily increase the solubility of the mineral matter held in combination, as it is generally conceded that the organic constituents of the soil in its natural state are quite insoluble in water and acids, more especially the former. There is also evidence of the existence of fatty or resinous organic matter which would materially affect the properties of the soil film. For the decomposition of such bodies it would be necessary to heat the soils considerably above 100° C.

In addition to the above-mentioned effects of heat the relation between solid and solvent would naturally be affected by other factors. Among these, would be absorption or "fixing power" of the soil.<sup>2</sup> It is reason-

able to expect soils with widely varying physical and chemical properties, such as the samples used in this series, to vary widely in their absorptive power. Hence it is not at all unlikely that the lack of consistency in some of the results obtained is due primarily to this factor. Not only is there lack of uniformity in the absorptive power of soils but they also show considerable selective power in the absorption of mineral constituents. Soils high in humus should tend to have a high fixing power, due to the properties of this constituent of chemically combining with minerals as well as its power of absorption, and, therefore, the effect of heat upon highly organic soils should tend to increase the solubility of the minerals. This was found to be true in the highly organic soils of the series. Another factor is that of precipitation following extraction, being the more marked in the acid extract due to a more complete extraction.

In passing from 250° C. to ignition the effects are apparently of a specific rather than general nature, which have been previously discussed. Among these are the volatilization of certain sulfur compounds, conversion of bicarbonates into normal carbonates, dehydration of silicates, etc., replacing of potash by lime and other chemical transformations. In addition there is produced a greater aggregation of the soil particles, resulting in a decrease in surface area exposed to the solvent and an accompanying change in the fixing and absorbing powers of the soil. It is possible, by application of these conceptions, to explain the majority of changes, both increases and decreases in solubility resulting from ignition.

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HAWAII EXPERIMENT STATION  
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#### THE USE OF SODIUM CITRATE FOR THE DETERMINATION OF REVERTED PHOSPHORIC ACID<sup>1</sup>

By ALFRED W. BOSWORTH

In 1871, Fresenius, Neubauer and Luck<sup>2</sup> published a method for the determination of reverted phosphoric acid in phosphates which involves the use of a solution of neutral ammonium citrate, specific gravity 1.09. This method, with a change in the temperature of the solvent, has been in constant use since that time<sup>3</sup> with no attempt by any one to give an explanation of the chemical reaction involved. It has been quite generally believed that the neutral ammonium citrate solution possesses a selective power which enables it to separate dicalcic-phosphate from tricalcic-phosphate. This is not true, for it has been found in this laboratory that 100 cc. of the Official ammonium citrate solution<sup>2</sup> is capable of dissolving 1.3 grams of precipitated tricalcic-phosphate in one-half hour at a temperature of 65° C. This dissolving of the tricalcic-phosphate is accompanied by a precipitation of calcium citrate.

<sup>1</sup> Read before the Association of Official Agricultural Chemists, Washington, D. C., Nov. 17, 1913.

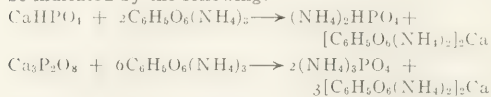
<sup>2</sup> *Z. anal. Chem.*, **10**, 133.

<sup>3</sup> U. S. Dept. Agr., Bur. of Chem., *Bull.* **107** (revised).

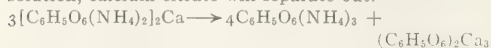
<sup>1</sup> King (*loc. cit.*) in discussing the relative solubilities of fresh and dried soils advanced this idea.

<sup>2</sup> Richter (*Landw. Vers. Stat.*, **47** (1896), p. 269) found that heating the soil increased the absorptive power of the soil for water.

This separation of calcium citrate led to the belief that the solvent action of the citrate solution was the result of a double decomposition started by the free phosphoric acid always present in an aqueous solution which is in contact with a solid phase composed of a phosphate.<sup>1</sup> This double decomposition might be indicated by the following:



If appreciable amounts of calcium are taken into solution, calcium citrate will separate out.



A great deal of work has been done upon methods of making neutral ammonium citrate solutions and several such methods have been published. The fact that neutral ammonium citrate is very unstable and easily loses ammonia has not been sufficiently considered in this connection, however. Why should extreme care be taken to secure an absolutely neutral solution, if this solution is to lose ammonia when heated a few degrees above the room temperature? Most chemists who have used the neutral ammonium citrate solution know that ammonia is constantly given off during the half hour allowed for the solvent action to take place. The final result then, is not the action of neutral citrate but rather the action of an acid citrate. There seemed to be no theoretical reason why a solution of sodium citrate should not be just as effective a solvent and it possesses two distinct advantages. It is a more stable salt and as the base in it is not volatile the solution would remain neutral throughout the whole operation. All trouble in securing a neutral solution would be eliminated, for a solution of citric acid could be neutralized with sodium hydroxide, using phenolphthalein as an indicator, or the neutral crystals of sodium citrate could be dissolved in water, and the solution made up to the required volume.

In order to learn what the action of a solution of sodium citrate might be, one was made which was of the same molecular concentration as the Official<sup>2</sup> ammonium citrate solution, *i. e.*, 314 grams crystallized sodium citrate,  $(\text{C}_6\text{H}_5\text{O}_6\text{Na})_2 \cdot 11\text{H}_2\text{O}$ , per liter. This solution was used to determine the amounts of insoluble and reverted phosphoric acid in several fertilizers, Thomas slag, ground bone, ground rock phosphate, dicalcic-phosphate,  $\text{CaH}_2\text{PO}_4$ , and tricalcic-phosphate,  $\text{Ca}_3(\text{P}_2\text{O}_7)_2$ . The results, together with those obtained by the use of the Official citrate solution, are given in the table.

In connection with these figures, it is noticeable that the differences between the figures obtained with the two solutions are, in most cases, of the same magnitude as the variations in the figures obtained by different chemists working upon the same sample.<sup>3</sup> It is also interesting to know that Samples 5, 10 and 11, which show the largest differences, all contain bone. The duplicate determinations, in all cases, showed

closer agreement with sodium citrate solution than with the Official citrate solution.

The Official method directs that the flask in which the reaction takes place should be loosely stoppered, during the time it is being maintained at 65° C., in order to prevent evaporation. The use of stoppers often results in the loss of a determination through the breaking of a flask. It is suggested that the flask be closed with a one-hole rubber stopper carrying an empty calcium chloride tube, 300 mm. in length, which will serve as a condenser. The use of such a condenser will not interfere with the shaking and it furnishes a vent which prevents the breaking of the flask.

The last column of the table shows the amounts of ammonia given off during the half hour of treatment with ammonium citrate solution prescribed by the Official method. This ammonia was caught in standard acid by means of an air current which was passed through the Erlenmeyer flask in which the solvent action was taking place. These figures seem to bear some relation to the difference given in the preceding column. By noticing the large amounts of ammonia given off by the Thomas slag, rock phosphate and ground bone when treated with ammonium citrate at 65° C. for one-half hour an indication as to the reason for the liberation of the ammonia may be found. The fertilizing materials, after being extracted with water, leave a residue which, in most cases, contains alkaline material, alkaline phosphates, carbonates of calcium and magnesium and oxides of other elements. These all tend to drive off ammonia from the citrate solution.

COMPARISON OF THE USE OF AMMONIUM CITRATE AND SODIUM CITRATE FOR THE DETERMINATION OF REVERTED PHOSPHORIC ACID

	Total P <sub>2</sub> O <sub>5</sub>	Water-soluble P <sub>2</sub> O <sub>5</sub>	By ammonium citrate		By sodium citrate		Difference	C <sub>2</sub> of N <sub>2</sub> liberated in 1/2 hour at 65° C.
			Insol. P <sub>2</sub> O <sub>5</sub>	Reverted P <sub>2</sub> O <sub>5</sub>	Insol. P <sub>2</sub> O <sub>5</sub>	Reverted P <sub>2</sub> O <sub>5</sub>		
1	10.63	6.18	1.75	2.76	2.61	1.84	0.91	14.9
2	8.73	3.76	1.42	3.55	1.89	3.08	0.47	12.7
3	9.58	6.50	0.76	2.32	1.11	1.97	0.35	10.9
4	12.33	11.90	0.02	0.41	0.00	0.43	0.02	6.5
5	14.59	1.21	4.01	9.37	9.07	4.31	5.06	12.5
6	10.92	3.76	0.58	6.58	1.11	6.05	0.53	13.5
7	11.18	8.73	0.34	2.11	0.66	1.79	0.32	16.0
8	9.61	4.24	1.62	3.75	2.80	2.57	1.18	14.2
9	7.31	0.95	2.59	3.77	4.58	1.78	1.99	10.5
10	8.79	0.00	5.22	3.57	7.78	1.01	2.56	29.0
11	19.91	1.84	6.34	11.73	14.89	3.18	8.55	23.0
12	13.07	8.42	0.22	4.43	0.77	3.88	0.55	13.5
13	11.69	4.33	3.68	3.68	4.15	3.21	0.47	16.9
Bone	20.95	0.00	13.36	7.59	15.82	5.13	2.46	14.0
Rock phosphate	17.57	0.00	9.40	8.17	15.69	1.88	6.29	65.0
CaH <sub>2</sub> PO <sub>4</sub> } 1 gram			0.00		0.00		0.00	3.5
Ca <sub>3</sub> (P <sub>2</sub> O <sub>7</sub> ) <sub>2</sub> } taken 1			0.00		0.00		0.00	14.0
Ammonium citrate heated to 65° C.								2.6
Ammonium citrate heated to 75° C.								36.0

It is realized that the small amount of evidence presented in this paper does not settle the question as to the desirability of substituting sodium citrate for ammonium citrate in the determination of reverted phosphoric acid. The subject is simply brought forward at this time in order that those chemists who are interested may give it some thought.

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<sup>1</sup> Cameron and Hurst, *Jour. Amer. Chem. Soc.*, **26**, 905.

<sup>2</sup> U. S. Dept. Agr., *Bur. Chem.*, Bull. **107** (revised).

<sup>3</sup> *This Journal*, **3**, 118 and **5**, 987. The differences between the extremes in these two cases are 1.23 per cent and 0.90 per cent, respectively.



# LABORATORY AND PLANT

## APPLICATIONS OF OZONE<sup>1</sup>

By A. VOSMAER

Ozone is generated by the action of the so-called brush discharge<sup>2</sup> on oxygen, the product being ozone more or less diluted with either non-converted oxygen or air, the latter being the rule in actual practice. Though the use of pure oxygen gives a higher concentration of ozone, this increase is not sufficiently high to justify the high cost of the gas. In laboratory apparatus the concentration of ozone can be run up as high as 160 grams per cubic meter, but in regular work on a larger scale it is hardly possible to get more than something like 30 and even that is rather high.

Since the cost per gram of ozone is not a linear function of the concentration, but increases rapidly with concentration, it is fortunate that ozone possesses such wonderful oxidizing powers that concentrations very much lower than those cited are quite sufficient for most purposes. For the manufacture of ozone there are now several ozonators of varying values on the market<sup>3</sup> and it is necessary to obtain the right kind for the purpose in mind, as it would be wasteful to generate a high concentration ozone and afterwards dilute it with air. Nearly all ordinary work can be done with a concentration of between 3 and 5 grams per cubic meter; a very large amount of work can be satisfactorily carried out with ozone of no more than about one gram, and some special applications require far less yet, down to two-tenths of a milligram, so that there is ample variety.

The only property of ozone that is of commercial importance is its remarkably strong oxidizing power, unless we consider its wonderful power as a germicide to be due to a specific property. I am inclined to do so, but there is evidence also that its germicidal value can be traced to its oxidizing power.

Before discussing the applications of ozone in detail, I wish to draw attention to some important points which govern the ozone industry: (1) Ozone is scarcely soluble in water—some say it is absolutely insoluble, which would be very improbable; others claim its solubility to be about ten times that of oxygen which latter statement seems as improbable as the former. (2) Ozone is difficult to make and when made, is difficult to keep; in fact, there is no storage question, the ozone being used when made. (3) As the gas may be considered hardly soluble at all in the ordinary sense of the word, molecular contact between ozone and the substance to be treated fails and one has to make up for it by long and very intimate mechanical contact which in practice means a special apparatus and constitutes the engineering part of the business.

A great advantage when using ozone is that its product of decomposition is a gas which is easily separated from the material that has undergone the treatment, and with which we are all familiar. It is a matter of diversity of opinion, and open to discussion,

whether or not ozone when acting splits off one active atom or utilizes all three. In my opinion it is probable that it is all three.

## PURIFICATION OF WATER

Years ago this most important of the possible applications of ozone originated in Holland where non-success in the sterilization of milk lead to successful sterilization of water. The interest of German scientists was soon aroused, and Frohlich of the firm of Siemens and Halske took up the work. Unfortunately, the Hollanders (Tindal and Schneller) ultimately, through lack of pecuniary funds, got on the wrong track and the business failed, not because ozone did not do the work but because Schneller did not know how to handle it. To Tindal anyhow belongs the honor of having done pioneer work in this line and later success surely owes much to his attempts.

It takes very little ozone to purify water of ordinary quality, but success depends to a large extent on the apparatus used for the purpose, not only as regards efficiency, but also with reference to purification. It is here that the time factor comes in. To accomplish purification and eventually the complete sterilization of water, it is necessary to have the water in close contact with the ozone, and to keep it so for several minutes. This is the whole secret of the work but the time factor was generally overlooked in the early attempts.

The ideal apparatus for the treatment of liquors with gases is not at all the well known scrubber, though this is used to a large extent for that purpose. In the ordinary scrubber, whether made of baffle plates or filled with coke or pebbles, the only method of obtaining a sufficient time of contact between liquid and gas is to make the apparatus so high as to increase the time required by the liquid to reach the bottom when let in at the top, but the upward stream of gas has a speed of its own which cannot be altered; this kind of apparatus does well enough for processes in which absorption is the object, but it has been introduced also in ozone applications and that was a mistake resulting in inefficiency.

The principle of the apparatus I have worked out is shown in Fig. 1. Here the water inlet is at the top and the outlet at the bottom, the reverse being the case for the ozone. By checking the outlet by means of an ordinary valve, the amount of water passing through in a given time can be regulated perfectly up to the maximum; the ozone entering through 3, passes a screen or perforated plate, 5, and then goes upward until it reaches the free outlet at 4. Another perforated screen at 6 serves the purpose of absolutely preventing even the smallest particle of ozone from escaping at the bottom before it has done its work. The height of the standpipe depends upon the quality of the water to be ozonized; if it be a bad water the time of contact has to be longer than with a water of good quality, quality in this particular case referring only to the content of organic matter in solution. Of course, one would expect the height to be greatest in the case of bad water, but that is not the case; on the contrary, there is another way of prolonging the time of contact,

<sup>1</sup> Abstracted by the author from a paper presented at the 6th Annual Meeting of the American Institute of Chemical Engineers, The Chemists' Club, New York, December 10-13, 1913.

<sup>2</sup> *Mt. Chem. Eng.*, **11** (1913), 623 and 705.

<sup>3</sup> *Ibid.*, **12** (1914), 36.

*viz.*, by means of increase in diameter. For bad water, evidently, far more ozone is needed than for a good water; this fixes the diameter of the standpipe, because in order to have it work perfectly, it is absolutely necessary that the whole cross area shall be completely filled by a homogeneous mass of gas and water with practically none but surface films of water surrounding the gas bubbles. The downward motion of the water checks the upward motion of the ozone to any desired extent, the natural buoyancy of a bubble being one factor in its movement and the downward force of the water the other. In actual practice this standpipe has to have a height of some 20 or 30 feet and may be made of any suitable material, even iron when properly coated.

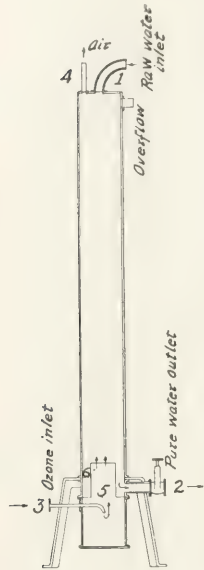


FIG. I

There are some interesting details concerning this apparatus: (1) The curious fact that its utter simplicity appeals to nobody unless it is seen in operation. I therefore used to build one of glass so as to show the whole affair outside and inside. Then the fact is evident that as long as there is sufficient pressure in the compartment under the screen 5, there is no chance for any drop of water entering; and the reverse happens at the screen 6 where the water alone passes through. This is easily explained by the assumption that a liquid and a gas cannot simultaneously pass through small openings; at 5 there is excess of gas pressure that causes the gas to take the lead; at 6 there is excess of water pressure which takes advantage of its position, the gas bubbles having no speed at all there. (2) Another thing that used to cause great surprise is that when started for the first time there is one big bubble, say one cubic foot in size, that enters into the water column but after having traveled for about 3 or 4 feet, it is entirely split up into small bubbles, the ordinary size being about one-quarter of an inch in diameter. This phenomenon, strange as it looks at first sight, is not at all extraordinary. It is entirely analogous to the fact that a vertical stream of water will invariably split up into drops; no matter what the initial size of the stream—the result is individual drops due to the surface tension of the water; in the case of the ozone the same surface tension of the water causes the enclosed gas bubbles to be of a definite size.

The apparatus described is what I would like to call perfect itself. In actual use on a larger scale it can be very conveniently altered so as to be even simpler. Instead of the inlet at the bottom through a perforated screen one can as well have a pipe come down

from the top until it reaches the bottom, the whole being then more like the old-fashioned wash bottle of the chemical laboratory. I may add that I have built these sterilizing towers of different sizes, from 6 inches in diameter to 6 feet, and from 10 feet in height up to 45 feet. In all cases the economical results have been entirely satisfactory. I claim an efficiency of 99 per cent for this apparatus, the average time of contact being four minutes.

As in commercial treatments on a large scale there is necessarily an excess of the reagent, so here it is preferable to have a slight excess of ozone for certainty of results. The excess escapes at the top freely and is too slight to pay for the trouble of recovery. This detail at once proves the advantage of this style of apparatus over the scrubber. I use no more than 1 gram per cubic meter; others use 2.5 grams and as the extra concentration of ozone is not used up in the short time of contact, there is a severe loss if the excess is not recovered. The germicidal power of ozone on water is of such strength that it does not require more than one gram of ozone to treat one million grams (1 cu. m.) of water of medium quality. In a water carrying less than the equivalent of 10 milligrams of permanganate of potash, only about one-tenth this amount of ozone is needed to do the work.

Fig. II shows the bottom of a small sterilizer made of glass for demonstrational purposes, and Fig. III the whole standpipe 30 feet high and a larger size, encased to prevent freezing. I may add that I have never found the slightest difference in the amount of ozone required for purification of water in winter and that needed in summer. A one foot diameter standpipe, the size of the glass one, takes care of up to 30 cubic meters of water per hour, *i. e.*, about 8,000 gallons. I have dealt with this apparatus at length because it has given absolute satisfaction in all cases and because it is well adapted for various applications.

The problem of taking iron in solution out of water is one that often presents itself on the other side of the ocean; it can be carried out successfully by the use of air in an apparatus similar to the one just described; as shown by actual practice, the height need not be over 10 or 12 feet. A more difficult problem is to get rid of organic ferric compounds. This can be done in the same apparatus by use of ozone, the precipitated hydroxide of iron being removed by any of the well known methods.

It is quite remarkable that ozone, as a gas, actually burns up most of the organic matter in solution in water and also converts the ferric compounds to ferric hydroxide. As an additional advantage of the use of ozone for the purification of water may be mentioned the fact that any discoloration, odor or abnormal taste is removed so that the result of efficient ozone treatment is a water perfectly clear, pure, colorless and perfect from a bacteriological standpoint. Modern science does not require a water to be perfectly sterile when it has to be used for drinking. It is important to note that the dangerous pathogenic bacteria, more especially the typhoid bacillus and the cholera vibrio, have very little resistance and yield first of all to the action of

ozone. What may be left after treatment are such absolutely harmless species as the *b. subtilis* or the *b. mesentericus* and in some cases spores. Fortunately water does not carry any pathogenic spore-forming bacteria.

#### USE OF OZONE IN THE INDUSTRIAL ARTS

This subject is not so simple or so well investigated as the former. There have been various trials of ozone in different branches of chemistry, but a good many failed, probably because the experiments were not interpreted in the right way, probably through ignorance of how to apply the new agent, perhaps also in some cases because there was no real opportunity for ozone to supplant the old agent. Certainly the fact that ozone is too expensive has been a reason for non-trial or non-success, but practically the whole field lies open. Aside from some few isolated or un-

atom of oxygen. If my opinion is correct, and the ozone furnishes three active atoms, then 48 grams of ozone give us 48 grams of O atoms, whereas it takes 70 of chlorine to yield 16 grams of O atoms; this would be an advantage of nearly 5 to 1 for ozone, which would have to be divided by three if we must use 48 grams of ozone to yield only 16 grams of O atoms.

The advantage of chlorine over ozone however is evidently not its direct price, but the fact that for the making of ozone much electrical apparatus is required, whereas chlorine as hypochlorites can be bought in bottles or in barrels. Ozone, however, wins if we do not look solely at direct cost price, but also at quality of product. I have been treating paper pulp with ozone. The result was excellent in so far as concerns the maintenance of fiber, the ozone bleached showing a length of fiber of several times that of the chlorine bleached, but one should be very careful not to use a high ozone concentration, because strong ozone will destroy fiber just as does chlorine; the secret here lies in the proper application of a weak ozone. The bleaching of cotton fabric is even more delicate and the rule must be "Do not hurry." Beeswax is an article that is fairly high priced, and its price is considerably higher when white. The bleaching has been carried out with success but a high concentration of ozone is necessary and a long treatment must be used because there is much organic matter to be removed. The bleaching of sugar molasses solution on the other hand is very easy, but the sugar is inverted which bars this use of ozone. Its use for bleaching glue is also easy, but it deprives the glue of its sticking properties.

More success is to be expected from the use of ozone in the oil industries. Cottonseed oil when ozonized has lost its peculiar taste and smell, but a large amount of ozone must be used to get this result. Sandal wood oil responds more readily to treatment and can be deprived of its taste and bleached also.

The manufacture of white or rather colorless egg-white from blood is not so easy but I have been successful to a certain extent in this line. The bleaching of flour is not at all successful, probably because it has to be done in a dry state. The flour retains a peculiar and disagreeable taste after treatment. The manufacture of varnish from linseed oil is a promising proposition, since the resulting varnish is of remarkable transparency because the oil has not been subjected to any high temperature. It may be that under favorable circumstances the drying of the oil, say for the manufacture of linoleums, may be advantageously done by means of ozone—the advantage in this case being a considerable shortening of time of the process.

The future of ozone is brighter than ever, but we must not exaggerate its importance. If we claimed to be able to sterilize milk or butter by it we would be making false statements. Neither do I believe in its value for aging wines. The flavor of wine is of such a delicate nature and the liability of its alcohol to acidify is so great that one cannot expect any beneficial effect in this line; we all know that even ordinary oxygen will spoil good wine in a couple of hours. What then can be expected of ozone? There are perhaps hundreds

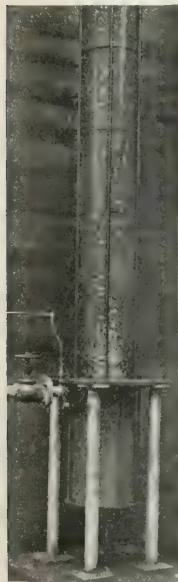


FIG. II

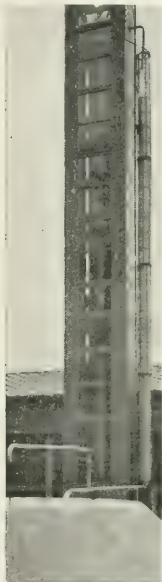


FIG. III

known instances, ozone has not yet entered the field of chemical industry, but it may do so at any moment.

Its use for bleaching purposes suggests itself first. It has to compete now with that very cheap and efficient agent, chlorine, either as a gas or in the form of hypochlorites of calcium, sodium or magnesium. This competition, solely a question of price per pound, is at present decidedly in favor of chlorine. Whether or not we shall be able to improve our present method of making ozone so as to increase the yield per kilowatt hour is now an open question. The theoretical yield is over a thousand grams and we are getting no more than 10 grams under the most favorable circumstances; hence, there must be a vast improvement before ozone can exceed any other bleaching agent in value. For the present we must accept the cost of ozone as it is—about 20 cents a pound. However, one must bear in mind that it takes two atoms of chlorine to give one



of possibilities for ozone, but I do not wish to speak of any with which I have had no personal experience. All my statements come from my own experience and are thus perhaps a bit one-sided, perhaps too enthusiastic, but that is the inevitable result of 15 years' work.

#### PURIFICATION OF AIR FOR VENTILATING PURPOSES

I wish particularly to call attention to the fact that I do not speak here of sterilization of air, but of purification. Dry ozone has no action whatever on dry air with its millions and millions of particles of dry dust. As a means of disinfecting a sickroom, ozone, even in strong concentration and moist, is not sensible. Besides bacteria clinging to the particles of dust, there are other sources of contamination. We must consider also volatile products of respiration, perspiration and other gaseous products.

What renders a crowded room disagreeable is not the carbon dioxide of the air nor lack of sufficient oxygen, but the odor due to the above named pollutions.

Even in a non-ventilated room there is plenty of oxygen for a long time for many people. Each breath takes but a trifling part out of the available total and what makes us feel uncomfortable is not the lack of anything but the excess of bad odors of organic origin. Now ozone is an extraordinarily powerful oxidizing agent and it will take care of these disagreeable odors, harmful not in the direct sense of the word but indirectly because one is liable not to breathe freely and deeply in an atmosphere that has a nasty odor.

Some people think that ozone only masks odors, but it is not very probable that a strong oxidizing agent like ozone would suddenly lose its power, and even if it should, the mere masking would be an advantage.

Dr. Franklin, in order to settle the question of masking *vs.* oxidation, has been carrying out some very interesting and conclusive experiments to which we can only refer.<sup>1</sup> His conclusions are absolute and convincing in favor of oxidation.

Of course, remembering the extremely powerful action of ozone and thinking also of the delicate character of our mucous membranes, it is an absolute necessity that the concentration of the ozone shall be an exceedingly low one—certainly not over one in a million parts of air and preferably something like one in ten million parts of air when intended for continuous breathing.

The question of purification of air with ozone is two-sided anyhow: (1) There is the purification of foul air and revivifying it by ozone; (2) there is the question of ozone as a therapeutic agent, *e. g.*, in cases of phthisis in its first stages, anemia, or obesity. I am not competent to give any statements regarding these diseases, but knowing that the inhalation of ozone in a very weak concentration actually does increase the percentage of oxyhaemoglobin in the blood, I believe that this fact, easy to control, should be sufficient to point to the

possibility of a beneficial effect. Even the chance of a possibility of doing something against tuberculosis should be an inducement for medical men to try so simple a treatment as ozone inhalation. As to the other side of the question, one should not lose sight of the influence of psychological conditions on physiological functions. We feel better in a room when there is no smell and to obtain that result we must ventilate to an extent far beyond the necessary replenishment of used up oxygen. What we really use ventilation for is to sweep out odors by large volumes of fresh air and if we can use ozone for that purpose we shall need far less fresh air for replenishment; this in winter means less expensive heating.

The problem of ventilation, however, is not such a simple one, as everybody who has to provide for doing it efficiently knows by experience. Sweeping out the used air has to be done by a large volume of new air which generally means a draft and usually the result is less efficient ventilation in order to avoid excessive drafts. If we try to express in grams the quantity of organic volatile matter present in a crowded space, we realize its smallness. In fact it sometimes does not amount to milligrams which explains the fact that ozone, one part in a million, is quite strong enough to take care of the destruction. We need no more than milligrams of ozone to do the work and it is a pity that unloyal objections to its use have been made, for in ozone we have a means of very cheap and efficient ventilation, since a hundred-watt apparatus will take care of the health of a large number of people. We may well remind the reader of the familiar example generally cited in text books on physics to illustrate the sensitiveness of our olfactory nerves. Asafoetida can be detected by its odor when present to the extent of one part in a thousand million million; this is an extreme case, but it is well known that it takes but very little of an odorless gaseous substance to be perceptible. In fact ozone itself is a good example since one part in ten million of air can be very easily noticed.

As to the amount of ozone required to purify the air in a room, it is safe to say that you should hardly perceive it. If there is a marked odor of ozone it proves that there is too much of it. It would do no harm, but some do not like it and from the business man's point of view, it is a wiser policy not to overdose the quantity, and thereby avoid complaints. Some people think ozone will never be used as a therapeutic because all of it is destroyed long before it has reached our lungs. I do not share that opinion for my personal experience goes to show that there actually is an increase in the oxyhaemoglobin percentage and that can be the case only when the ozone is not entirely absorbed by the mucous membranes that it passes on its way to the lungs.

In conclusion I wish to state that the actual applications of ozone are few, but the possible applications are numerous. Ozone can be had now in any quantity and quality and for a price that in many cases is less than that of other oxidizing agents.

<sup>1</sup> "Ozone in Ventilation," *Heating and Ventilation*, 10, Pt. 1, 30-35 and Pt. 2, 13-18.

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# A NEW VISCOMETER FOR GENERAL SCIENTIFIC AND TECHNICAL PURPOSES<sup>1</sup>

By EUGENE C. BINGHAM

Received November 25, 1913

Bingham and White<sup>2</sup> have already published a description of a viscometer with which absolute viscosities can be measured with very great certainty. This form of apparatus is easily made, but since the dimensions of the apparatus must be accurately known for absolute measurements, the time consumed in the calibration is considerable. So for general purposes it is preferable to calculate the *absolute viscosities* from *measurements* which are only *relative*. By this procedure not only is the calibration simplified but the apparatus itself may be made simpler and less delicate to handle.

It will be urged that viscometers in great number have already been devised for relative measurements. Why another one? The answer is that relative measurements are comparatively valueless unless the results can be calculated to absolute units. It has been supposed that the relative measurements obtained by the use of instruments of the Ostwald type might be calculated to absolute units without difficulty. This is not generally true and the reason is not far to seek. In the viscosity formula for calculating absolute viscosities<sup>3</sup>

$$\eta = \frac{st}{s \phi \theta}$$

which seems to be almost universally used, no account is made of the loss of the kinetic energy of the liquid within the capillary, this energy disappearing outside of the capillary without helping to overcome viscous resistance within the capillary. Furthermore, it can be shown<sup>4</sup> that this correction does not come into the calculation in such a way that it may be made to disappear. Viscometers of the ordinary type are deficient because the pressure producing the flow through the capillary is not variable at will. The result is that with very fluid substances the kinetic energy correction becomes large unavoidably, and with rather viscous substances the time of flow becomes intolerably long, necessitating the use of several instruments. With a very long period of flow the difficulties due to clogging with dust particles become very great. Applebey<sup>5</sup> had shown that with varying pressures, the values of  $st$  in the above formula, for a particular liquid, are only constant when the time of flow is rather great—for his particular instrument of the Ostwald type, at least six minutes. But with such sluggish flow he found that "in spite of all precautions, the tubes frequently became contaminated with dust." The necessity of the knowledge of the exact specific gravity of the liquid at each temperature where a viscosity measurement is desired lessens the convenience

of this type of instrument. Both the unreliability and the inconvenience of these instruments may be avoided by using variable pressure.

## THE PROPER DIMENSIONS OF AN APPARATUS FOR MEASURING VISCOSITY

The question of the proper dimensions of the apparatus should merit more attention than is usually given to this subject. A study of the best viscosity data leads one to believe that an accuracy of one-tenth of one per cent can readily be attained. If one desires values with a smaller limit of error than one-tenth of one per cent he should undoubtedly make absolute and not relative measurements. There does not exist the necessary experimental data for standardizing and testing a relative instrument for such a high degree of precision. We, therefore, assume that a relative instrument may be depended upon only to one-tenth of one per cent and that until our data are amplified, the absolute method must be used for measurements of higher precision.

With a stop-watch reading to 0.2 sec. the time of flow may be made as small as 200 sec. The volume of flow should be small for the following reasons: (1) The velocity of the liquid within the capillary should be low in order that the kinetic energy correction may be kept from becoming inconveniently large. (2) The time of flow should be small in order to economize time, and in order that the temperature may be the more easily kept constant during the time of flow. (3) Small masses of liquid come to the temperature of the bath more quickly. (4) There is also an economy of material. The minimum volume of flow is determined by our ability to read the volume with the desired accuracy. This in turn is determined by the diameter of the constricted portions of the apparatus above and below the measured volume. If, however, the constricted parts have very small bore, the effect of capillary action becomes disturbing. In particular, very viscous liquids do not drain out of the capillary, a meniscus is formed bridging across the capillary and a pressure is set up opposed to that causing the flow and the results of the measurement are then quite valueless. The troubles due to bad drainage may be minimized by having the drainage surfaces everywhere as nearly vertical as possible. In other words the change from the constricted tube to the tube of larger diameter should be made gradually. A constricted part with a bore of 0.25 cm. would have a volume of nearly 0.05 cc. per centimeter of length. Assuming that as the meniscus passes the marks, it can be read to 0.01 cm. it is only necessary to have a volume of 0.5 cc. but in order to provide a margin of safety in the construction and use of the apparatus, we have chosen 3 cc. as the volume of flow.

Testing for any error due to faulty drainage is easily accomplished. It is only necessary to test the flow of the most viscous liquid to be measured, using very different rates of transpiration. Lack of perfect drainage will show itself by the substance appearing to be more viscous at the lower rate of flow. Generally the more viscous liquids must be allowed to flow

<sup>1</sup> Twentieth communication bearing on this subject. Cf. *Physical Review*, **35** (1912), 407. *Ibid.*, N. S. **36** (1913), 96; *Z. physik. Chem.*, **83** (1913), 641; *J. Chem. Soc.*, **103** (1913), 959; *J. Physical Chem.*, Feb. (1914).

<sup>2</sup> *Z. physik. Chem.*, **80** (1912), 670.

<sup>3</sup>  $\eta$ ,  $s$ , and  $\theta$  represent the viscosity, density and time of efflux of the liquid which is taken as standard.  $\eta$ ,  $s$ , and  $\theta$  are the corresponding quantities for the liquid to be measured.

<sup>4</sup> *J. Chem. Soc.*, **103** (1913), 959.

<sup>5</sup> *Ibid.*, **97** (1910), 2000.

slowly enough so that the drainage will be complete. In the test here given, the drainage may conceivably appear to be perfect or even ultra-perfect. But this can be the case only when the flow begins with the meniscus of the liquid considerably above the upper mark, in which case the transpiration volume will be increased by a certain amount caused by drainage from the surfaces above the mark. This gain in volume will tend to offset the loss of a part of the transpiration volume which fails to pass through the capillary during the determination. Hence, it is highly advantageous to have the shape of the apparatus above the upper mark similar to that above the lower mark so that these effects may as nearly neutralize each other as possible.

The ends of the capillary are made trumpet-shaped in order to aid the drainage by avoiding horizontal surfaces and also in order to avoid the sharp corners on which filter shreds might get hung, causing clogging.

In making absolute measurements, it is customary to use a horizontal capillary. The theory for an inclined capillary is somewhat more complicated, but for relative measurements there appears to the author no reason against its use. There are some important advantages to be gained by the use of a vertical capillary. In the first place it is desirable to use a long capillary in order that the radius of the capillary may be relatively large and the kinetic energy correction relatively small and that any possible effects of the ends of the capillary may be negligible. Thus only with a vertical capillary may the limbs be kept close together, so that any small error in keeping the limbs exactly vertical will not so seriously affect the hydrostatic level in the instrument. Furthermore, the apparatus may be made stronger and more convenient to handle, and a smaller bath is required to hold it. It is not desirable to use a bent capillary, not only because of the unknown effect of the centrifugal forces but because of the danger of constrictions in the capillary at the bend. Since the velocity of flow varies as the fourth power of the radius, it will be greatly increased by a small constriction, and eddy currents will be formed at a relatively low rate of transpiration. The kinetic energy correction will also be correspondingly increased. Eddy currents cannot be tolerated even in a relative instrument and the kinetic energy correction should be kept low.

The pressure should be variable at will so that the time of flow may be kept reasonably constant. There need be no upper limit to the pressure, since liquids are practically incompressible. A pressure of 50 grams per sq. cm. can easily be read to 0.1 per cent on a water manometer, hence this may be taken as the lower limit.

As already pointed out, a long capillary is desirable, but since it is difficult to get a capillary of an exactly specified bore, it is best to pick a capillary of approximately the desired radius and then to cut the length to fit the other dimensions. Assuming that 20 cm. is a convenient length, Fig. 1 is given to show just what lengths should be taken from capillaries of different radius, the values being calculated by means of

equation (1), using the above dimensions  $t = 200$  sec.,  $p = 50$  grams per sq. cm., and  $V = 3.0$  cc. on the assumption that the highest fluidity to be measured is 500. There is no object in following the current custom of using a variety of viscometers in measuring liquids of considerably different fluidity. All that is necessary is to have a sufficient range of pressures at one's disposal. Of course, if one is not going to measure the viscosity of very fluid substances like ether

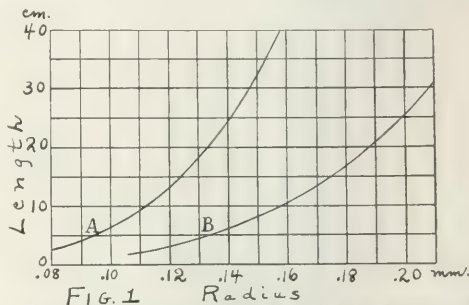


FIG. 1  
Lengths required from a capillary of given radius, assuming the minimum values  $\alpha = 1-200$ ,  $p = 50$ , and  $V = 3$ , (A), when the maximum fluidity to be measured is 500, and (B), when the maximum fluidity to be measured is only 125.

and hexane it may be best to construct an instrument which will require lower pressures, near the minimum of 50 grams given above, but this is purely a matter of convenience. In curve B of Fig. 1 we give the lengths required with capillaries of different radii on the assumption that the highest fluidity to be measured will be only 125 absolute units.

#### THE CONSTRUCTION OF THE APPARATUS

The appearance of the viscometer is shown in Fig. 2 as drawn to scale. The capillary is made in two parts EF and GH, from non-soluble glass. The transpiration volume is contained between the two marks B and D. In constructing the apparatus it is very important that the volume of C should be similar in shape, equal in volume to the volume K, and moreover, it is important that their centers of mass be as nearly as possible at the same elevation. This is done in order that the average resultant hydrostatic head of liquid within the instrument during the time of flow may be as nearly negligible as possible. It is also important that the volume AB should be equal to the volume HJ. As the viscometer is made of thin glass in order to facilitate the passage of heat a brace is put in between the right and left limbs of the instrument in order to strengthen it. This viscometer may be obtained from Eimer and Amend of New York.

A diagrammatic arrangement of the apparatus is shown in Fig. 3. The viscometer V is shown in a bath which also contains a thermometer, stirrer, etc. At M and N are two three-way cocks for connecting one limb of the viscometer to the pressure while the other is turned to air. After a measurement, the position of the cocks is reversed and a duplicate observation is made or both cocks may be turned to air. A drying device is shown at D, and a reser-



voir for keeping the pressure constant is indicated at *A*. For this purpose a large glass bottle<sup>1</sup> will serve, but particularly for the higher pressures an ordinary gas tank, wrapped in felt to keep the temperature steady, is convenient. The manometer *E* is conveniently filled with water but at the higher pressures mercury is required. It is best, therefore, to have two manometers, either of which may be connected to the pressure at will, but only one is shown in the figure. It has been found most convenient to read the manometer on a steel tape supported vertically against a strip of plate glass mirror. By bending both limbs of the manometer in such a way that the upper half of the right limb is directly above the lower half of the left and closed limb only one tape is required and the measurement is thus simplified. The upper part of the closed limb is prolonged upward so that all danger is obviated of the liquid in the manometer being drawn back into *A* or *D* when the pressure is removed. As shown in the figure, the pressure is obtained from a tank of compressed gas, *B*, but it may be obtained by means of an aspirator, a hand pump, or by means of a head of water. Generally it is necessary to have a check-valve, *F*, to hold the pressure once obtained. The right limb consists of tubing of very small diameter while the left limb is of large diameter. A little mercury at the bottom allows the easy passage of air to the left but not toward the right.

FIG. 2

In making viscosity measurements by the variable pressure method, it is neither necessary nor desirable to have every possible pressure at one's disposal. It is better to have only a few considerably differing pressures. It is desirable, therefore to have a device for giving constant pressures at the desired intervals. Such an arrangement is shown at *G*. The right limb is of large bore and contains a liquid through which the excess of gas rises in a fine stream. Other smaller pressures are obtained by allowing the gas to pass through the cocks 1, 2, or 3.

It is often desired to measure the viscosity of a liquid above its ordinary boiling point in which case the cocks *M* and *N* must not open to air at *P* but, together with the open end of the manometer, they must lead to a low pressure reservoir, *C*. The air in this reservoir is maintained at a constant pressure by means of the second pressure regulator *H* like that at *G*.

The dotted part of the apparatus is not essential to the manipulation under ordinary conditions. All of the parts except the viscometer and the manometer may be made of metal so as to withstand high pres-

ures, but glass tubing with rubber connections will serve for ordinary conditions.

If one is working at other than atmospheric pressure, it is unnecessary to add that another manometer is essential if the pressure within the reservoir *C* must be exactly known.

#### THE MAKING OF A VISCOSITY MEASUREMENT

After thorough cleaning, the apparatus is rinsed out with pure, dust-free water. If other liquids than water are to be introduced, dust- and grease-free alcohol and ether, and dry air which has been passed through cotton may be used for drying. The liquids may be regarded as satisfactory when dust particles cannot be seen when carefully examined in the direct rays of the sun.

The apparatus is then partially filled with the pure liquid to be measured, the liquid being introduced

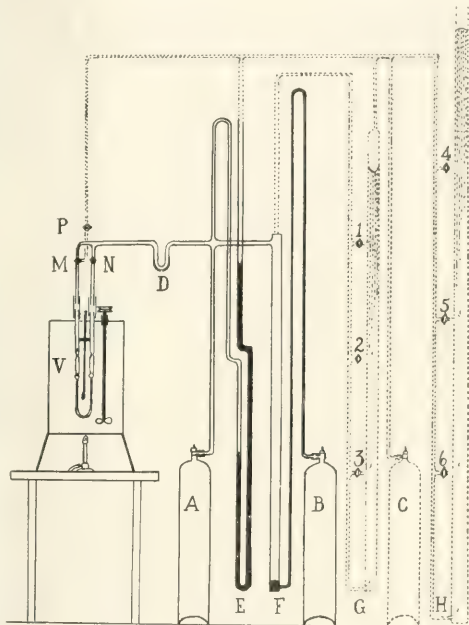


FIG. 3

into the right limb. Pressure is now applied to the right limb and as the liquid passes into the left limb care is taken that no bubbles remain in the apparatus. Finally the liquid runs over into the trap at *A*. Making sure that the temperature is adjusted properly, the liquid is allowed to run into the trap until the lower meniscus reaches exactly to the point *H*, when the pressure is removed, the cock *N* being turned to air. If much liquid is in the trap it may be removed. The remaining liquid in the apparatus is the "working volume," so-called by Thorpe and Rodger.<sup>1</sup> Keeping the temperature constant, the left limb is now turned to pressure and while the meniscus falls from *A* to

<sup>1</sup> Phil. Trans., 186A (1894), 397.

*B* the pressure and temperature of the manometer are read. As the meniscus reaches the point *B* the time record is begun and closed when the meniscus reaches the point *D*. The pressure and temperature are again read after which the left limb is immediately turned to air, before the point *E* is reached. The liquid is now in exactly the position for a duplicate reading in the reverse direction. On account of the change in volume on heating, it is necessary to adjust the working volume after each elevation of temperature.

It is evident that the duplicating observations in reverse directions will not be identical even if the pressure as read on the manometer is the same, unless the effective hydrostatic head within the instrument is equal to zero. In constructing the instrument it was intended to make this as small as possible, and by making a series of observations with a liquid of known specific gravity at constant pressure and temperature, it is easily possible as shown later to calculate the correction for any failure in the construction.

Naturally water is the liquid which one would select for the purposes of calibration. The viscosity of water is better known than that of any other liquid and for convenience the values obtained by several observers for the fluidity of water have been grouped together in Table I. It is important to emphasize

of water increases over 500 per cent from 0° to 100°. For very fluid liquids, ether and hexane are suggested, and for very viscous liquids cane sugar solutions.<sup>1</sup>

Finally, it needs to be remarked that a correction may be required for errors of thermometer and stop-watch. Particular care needs to be exercised to see that the stop-watch keeps *uniform* time. This can be tested by timing ten-minute intervals on a chronometer. Many stop-watches fail in this test and must be discarded. Temperatures must be read to the hundredth part of a degree.

#### THE CALCULATION OF MEASUREMENTS

The formula for calculating viscosity under the above conditions of measurement is

$$\eta = \frac{\pi g r^4 \rho}{8 V l} - \frac{m n \rho V}{8 \pi l} \quad (1)$$

where  $\pi = 3.1416$ ,  $g$  is the acceleration due to gravitation,  $r$  is the radius of the capillary in cm.,  $t$  the time in sec.,  $p$  the pressure in grams per sq. cm.,  $V$  the volume of flow in cc.,  $l$  the length of the capillary. The second term contains the correction for the loss of kinetic energy and it should always be but a small fraction of the whole, preferably less than one per cent. The number of capillaries is represented by  $n$ , while  $\rho$  is the density of the liquid under investigation, and  $m$  is a constant equal to 1.12.

For a given instrument the equation (1) becomes

$$\eta = C'p - C'/\rho \quad (2)$$

Since the second term is of comparatively small importance, the value of  $C' = mnV/8\pi l$  may be obtained by approximate measurement with sufficient accuracy. Knowing the values of  $p$  and  $\rho$  as well as the density and viscosity of the liquid used in standardization, the value of  $C$  may be readily calculated.

In obtaining the value of the pressure several corrections must be made: (1) The pressure in the manometer must be calculated in grams per sq. cm. from the known height of the liquid and the specific gravity of the liquid at the temperature observed; (2) This pressure must be corrected for the weight of the air displaced by the head of liquid in the manometer, and if the limbs of the manometer are very unequal in bore a capillary correction may be required; (3) Unless the surface of the liquid in the lower limb of the manometer is at the same height as the average level of the liquid in the viscometer, a correction must be made for the greater density of this enclosed air, which is under pressure, than of the outside air; (4) Finally a correction must be made for the average resultant hydrostatic head of liquid within the viscometer. If the two volumes  $C$  and  $K$  in Fig. 2 are exactly similar in shape, equal in volume and at the same elevation when the viscometer is supported in its vertical position, it is evident that the gain in head during the first half of the flow will be exactly neutralized by the loss in head during the last half of the flow. Since this is never exactly the case, a correction is made as follows: Duplicate observations in reverse directions are made upon a liquid of known density and viscosity at a constant pressure and tempera-

TABLE I—THE FLUIDITY OF WATER AT VARIOUS TEMPERATURES AS MEASURED BY DIFFERENT OBSERVERS

Temperature	Poiseuille (a)	Sprung (b)	Slottet (c)	Thorpe and Rodger (d)	Lyle and Hosking (e)	Bingham and White (f)	Average
0	56.3	56.3	55.3	56.2	55.8	55.9	55.9
5	66.0	66.2	65.6	66.2	...	65.6	65.9
10	76.3	76.9	76.1	76.5	76.4	76.9	76.6
15	87.3	88.1	87.4	87.9	...	87.6	87.7
20	99.2	99.7	99.2	99.8	99.1	99.4	99.4
25	111.5	111.6	111.6	112.0	...	111.8	111.7
30	124.8	124.7	124.5	125.4	124.7	125.0	124.8
35	138.7	138.3	138.1	138.9	...	138.3	138.5
40	153.1	152.2	152.2	153.2	152.2	152.4	152.5
45	168.1	166.1	166.1	167.4	...	166.8	166.9
50	...	180.8	180.8	182.4	180.8	181.8	181.4
55	...	...	196.1	197.8	...	196.9	196.9
60	...	...	211.9	213.7	211.9	211.2	212.1
65	...	...	228.3	229.5	...	228.9	228.9
70	...	...	245.1	246.3	245.7	245.4	245.6
75	...	...	261.8	263.5	...	262.8	262.7
80	...	...	279.3	280.5	279.4	280.1	279.8
85	...	...	296.7	298.3	...	298.7	297.9
90	...	...	314.5	316.8	316.5	318.2	316.5
95	...	...	332.2	335.0	...	334.0	333.7
100	...	...	350.9	353.4	350.9	...	351.7

a. *Mém. présent. par divers Savants à l'Académie Roy. des Sciences de l'Inst. de France*, 9 (1846), 433. Calculation by Thorpe and Rodger.

b. *Pogg. Ann.*, 169 (1876), 1.

c. *Wied. Ann.*, 20 (1883), 257.

d. *Loc. cit.*

e. *Phil. Mag.*, [6] 3 (1902), 487.

f. *Loc. cit.*

here that the testing of a relative instrument with only one liquid at a single temperature is entirely unsatisfactory. Such a procedure allows all sorts of errors to creep in without any means of detection. It is best to use several liquids and a variety of temperatures in the calibration and testing. The fluidity

<sup>1</sup> Cf. Hosking, *Phil. Mag.*, [5] 49 (1900), 274.

ture. Let  $t_1$  be the time of transpiration from left to right and  $t_2$  the corresponding time from right to left. Let  $p_0$  be the pressure, corrected except for the average resultant head of liquid in the viscometer. Let this head be equal to  $x$  centimeters of liquid as the liquid flows from left to right, so that in this case the total pressure becomes equal to  $p_0 + \rho x$  but when the liquid flows from right to left the pressure must be  $p_0 - \rho x$ . From equation (2) we obtain the following equations.

$$p_0 + \rho x = \frac{\eta + C'\rho/t_1}{Ct_1} = \frac{\eta}{Ct_1} + \frac{C'\rho}{Ct_1^2}$$

$$p_0 - \rho x = \frac{\eta + C'\rho/t_2}{Ct_2} = \frac{\eta}{Ct_2} + \frac{C'\rho}{Ct_2^2}$$

whence

$$x = \frac{\eta}{2C\rho} \left[ \frac{1}{t_1} - \frac{1}{t_2} \right] + \frac{C'}{2C} \left[ \frac{1}{t_1^2} - \frac{1}{t_2^2} \right]$$

In obtaining this correction term it is sufficient to use the approximate value of  $C$  obtained by using equation (2) with  $p_0$  in place of  $p$ . In subsequent calculations it is necessary to know the specific gravity of the liquid to be measured in order to make the necessary pressure correction and also in order to make the kinetic energy correction, but it is to be noted that if the construction of the viscometer and the measurement has been properly done these correction terms will both be small; hence, the specific gravity need be only approximately known, which constitutes a great advantage of this method.

If the viscometer is constructed of the same material throughout, the coefficient of expansion of the material need not be taken into account, as may be easily verified by introducing the coefficient of expansion into the dimensions in equation (1). But we cannot legitimately assume that the same is true of any changes in the dimensions of the apparatus due to the solubility of the glass. For this reason the time of flow of the liquids used in calibration should be redetermined occasionally. However, so far as is known to the author, the most prolonged use of a given instrument has never yet shown a change in the time of flow which could be attributed to this cause.

In conclusion, we believe that this viscometer is capable of a higher degree of precision than the forms usually employed and that at the same time it is easily made, convenient to use, and economical of time. The corrections which have been discussed are small in this type of apparatus, so that the calculation of the viscosity by means of equation (2) is simple.

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### MODIFIED HEMPEL PIPETTES

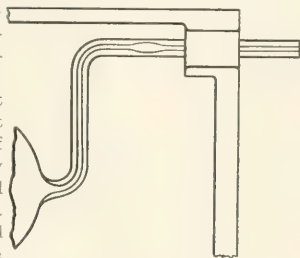
By R. P. ANDERSON

Received November 7, 1913

The chief objection to the present form of the Hempel pipettes lies in the fact that small drops of the reagent collect in the capillary while the gas is in the pipette and are carried over into the burette on the return of the gas. This causes no appreciable error when water is used as the confining liquid, but is ob-

jectionable on account of the unsightly appearance that it gives to the burette and on account of the frequency with which the water must be changed. However, when mercury is used as the confining liquid and, as is usually the case, a small amount of water is placed on its surface, contamination of this water by the reagent will result in a change of the tension of aqueous vapor, and may influence to a measurable extent the volume of the gas.

For example, let it be assumed that there is 0.1 cc. of water on the mercury in the burette and that about 0.013 cc. of alkaline pyrogallol is carried into the



burette during the absorption of oxygen. Since this reagent contains at least 0.8 gram of potassium hydroxide per cc. of solution, the resulting liquid in the burette will be approximately a 10 per cent solution of potassium hydroxide. At 20° C., the vapor pressure of water is 17.53 mm., and of a 10 per cent solution of potassium hydroxide, 16.38 mm. On the basis of 760 mm. as the total pressure of water vapor and gas sample, the percentages of water vapor by volume are, respectively, 2.31 and 2.16. At 25° C., the vapor pressures are 23.76 mm. and 22.19 mm., and the percentages by volume, 3.13 and 2.92, respectively. Therefore the error in volume caused by the presence of this amount of potassium hydroxide in the water would be 0.15 per cent at 20° C., and 0.21 per cent at 25° C.

The change in the volume of a gas sample that is caused by this contamination with reagent of the water in the burette depends, of course, upon the reagent in question and upon the care that is taken in the manipulation. In the hands of an experienced gas analyst, the error need never be as large as 0.1 per cent, but oftentimes, especially in student's work, it becomes as large as that of the preceding example.

In attempting to modify the pipettes so that the reagents would be largely retained in them during the return passage of the gas, an enlargement 3 mm. in diameter was made in the capillary tube of each pipette just below the upper horizontal portion of the frame. This enlargement serves as a trap for the small drops of reagent that are carried up to it and since the amount of reagent that collects in the capillary tube between the enlargement and the tip of the burette is small, very little, if any, reagent is carried over into the burette. However, since there is no advantage in the U-shaped capillary tube of the usual form of the Hempel pipette in the present method of manipulation<sup>1</sup> and since its presence increases the amount of reagent that must be retained in the trap, the pipettes were finally constructed as shown in the accompanying figure. This modification is the one that is being used in the Cornell laboratory at the present time on the absorption pipettes. The combustion pipettes are similarly constructed with the exception of the

<sup>1</sup> Dennis' *Gas Analysis*, pp. 59-64.



enlargements. The length of the horizontal portion of the capillary tube is such that the pipette fits in the frame designed for the original form. This horizontal portion can be shortened somewhat by bringing the first bulb of the pipette over to the left edge of the pipette frame and changing the form of the frame accordingly. It was not thought desirable to extend the capillary tube in a vertical direction<sup>1</sup> from the first bulb of the pipette since that would necessitate the use of a longer capillary in making the connection with the burette.

These pipettes are furnished by Greiner and Friedrichs, Stützerbach in Thüringen, Germany. In ordering, emphasis should be laid upon the *actual* size of the enlargement, since on account of the magnifying action of the glass, an enlargement *apparently* 3 mm. in diameter is considerably less than that, and is not as satisfactory as the larger one.

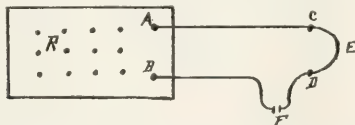
CORNELL UNIVERSITY, ITHACA, N. Y.

### AN EFFICIENT METHOD FOR CUTTING GLASS

By J. I. HARDY

Received December 8, 1913

There is often great difficulty in satisfactorily cutting glass in the scientific laboratory, and this is especially true in the case of glassware of large diameter. There are several methods in common use. Probably the fine flame of the blowpipe applied upon a file scratch is one of the best known methods. The diamond point is often used with satisfaction. A metal rod may be bent to the shape of the object to be cut, heated red hot, and passed over the surface on the line where the glass is to be cut, then if the glass is plunged into water it will separate on this line of contact. There is a method by Kunz,<sup>2</sup> using an electrically heated nickel wire on a rather complicated apparatus which requires an electric current of about



eleven amperes. In this method a few drops of water are applied to the heated glass, causing it to crack.

The writer believes the following method to be capable of wide application, and that the desired results can be rapidly and efficiently obtained in the average laboratory. The equipment consists of an electric system giving at least six amperes electric current, a resistance apparatus consisting of a rheostat or a bank of twelve lamps (16 c. p.) arranged in parallel, and a piece of No. 24 nickel-chromium wire. When long tubing is to be cut, a steady rest will prove helpful and can be arranged to suit the convenience of the operator. The method of procedure is as follows:

Bind a piece of wire around the glassware, twisting the ends together and making sure that the wire follows the line where the glass is to be cut. This wire serves only as a guide, and may be of any inexpensive

material. In the diagram, *R* indicates the bank of lamps, which is used on account of being both inexpensive and easily adjusted to definite resistance. At binding posts *A* and *B* connection is made with the electric light system of the building. Between *C* and *D* is inserted the No. 24 nickel-chromium resistance wire *E*, and *F* is the switch.

After the lamps *R* are loosened sufficiently to break their connection, the switch at *F* is turned on, and the lamps are screwed in one at a time until the wire *E* is a dull red. The glassware which has been prepared with guide wire is given a slight file scratch of about one-quarter inch length on the line to be followed in cutting, and is brought into the loop *E* and revolved two or three times, holding the nickel-chromium wire



- 1—Graduated Cylinder, cut above 1 L. mark.
- 2—2.5 L. bottle. 3—Similar to 2.
- 4—2 L. Erlenmeyer Flask.
- 5—Battery Jar, cut 1 1/4 in. below break.
- 6 and 9—Jena beakers, 1 L. and 150 cc.
- 7—Brittle Thin-walled Tubing, poor grade of glass.

close to the metal guide. After the glassware has been revolved two or three times in the loop *E* more lamps are connected in the bank *R* until the wire *E* is a bright red. Now the wire loop *E* is held in contact with the file scratch for a few seconds until a crack is started. The glassware is now revolved, keeping the heated wire slightly ahead of the crack until the glass is cut off. If the wire cools it may be released slightly from the glass until it regains its heat.

This method is very effective and can be used to cut any kind of glass from cheap bottle glass to the best Jena. It will work successfully on glassware with cylindrical, spherical or conical walls, and will cut the glass in any direction in which the guide is placed. A 2 1/2 liter bottle was split (after having its neck cut off) horizontally, although it required more time than any of the ordinary glass-cutting problems because of the thickness of the bottom of the bottle.

The accompanying photograph shows nine samples which were cut by this method in about one-half hour.

AGRICULTURAL EXPERIMENT STATION  
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### APPARATUS FOR TAKING DUST AND BACTERIA SAMPLES OF AIR

By CHARLES BASKERVILLE  
Received February 12, 1914

In the investigation<sup>1</sup> of the air of the schoolrooms of New York City, carried on with Professor C.-E. A. Winslow at the request of the School Inquiry Committee of the Board of Estimate and Apportionment, it early became apparent on account of the large num-

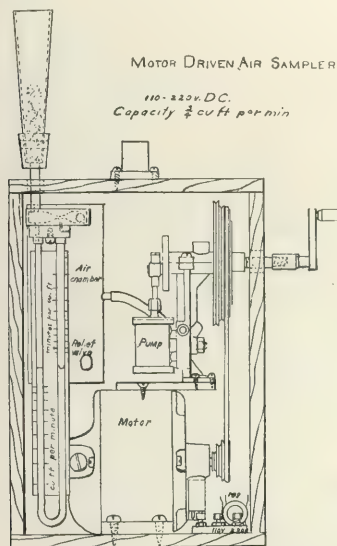
<sup>1</sup> See White and Campbell, *J. A. C. S.*, **27** (1905), 734.

<sup>2</sup> *Chem. Ztg.*, **37**, 406-407.

<sup>1</sup> See *This Journal*, this issue, p. 251.

ber of samples to be collected, in widely separated schools perhaps on the same day, that it would be necessary to depend upon some other method than one relying upon the use of a hand pump in conjunction with a gas meter. The limited time per day (school hours) available for collecting samples and the transportation of apparatus were factors of supreme importance.

After many conferences, in which the entire staff took part, Messrs. Wallace and Tiernan, Engineers,



New York City, who also had a representative present, supplied us with an apparatus, which we think should be described for the benefit of those members of the Society interested in atmospheric hygiene.

The principle of the apparatus depends upon measuring volume by time. The apparatus includes an exhaust pump of the friction type run by a  $\frac{1}{32}$  horse power motor and a measuring apparatus of compact and ingenious design. This apparatus, placed be-

tween the pump and the sampling filter, consists of an air chamber, the inlet of which is connected with the two ends of a U-tube, graduated on its distal arm. The opening of this distal arm is so reduced that the pressure at the mouth of the proximal arm is registered by a rise of the liquid in the distal arm. The whole apparatus is enclosed in an oak box fourteen inches by twelve inches, air being drawn in through an opening at the top and forced out through an opening in the side. The upper opening is fitted with a small steel cup with a rubber stopper inside, having a hole large enough to fit the constricted end of the sugar or sand filter. At the base of the cup, an extension passes through the wooden cover and screws on to the suction chamber of the machine.

The apparatus as first made was designed to draw through about three-quarters of a cubic foot of air per minute. With the resistance due to the sand or sugar, however, the time required was about three minutes per one cubic foot. The pump when first tested proved to be too noisy, so the apparatus was placed within a second box lined with felt and a muffler attached to the exhaust. This reduced the noise to a minimum. Teachers in whose classrooms we operated, were consulted, and no objections were offered to the noise made by the apparatus during class hours.

The accuracy of obtaining dust and bacteria samples by means of this form of apparatus was compared with the hand pump and meter method and approximately similar results were obtained. A further check was made by running the electrically driven pump and measuring the flow by means of standard gas meters. Both the electrical pump and the gas meters were tested and standardized by the manufacturers.

The amounts of air taken for samples for bacteria and dust with this machine were usually three feet and two feet, duplicate determinations always being made. The official methods of the Public Health Association were used in making counts of bacteria and studying the character of the dust collected.

The apparatus might be used extensively in studying the air of factories and other places where occupational diseases are to be investigated.

COLLEGE OF THE CITY OF NEW YORK

## ADDRESSES

### RECENT DEVELOPMENTS IN COMMERCIAL EXPLOSIVES<sup>1</sup>

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The last few years have seen a great development in the use of safer explosives than were previously commercially available or even believed to be possible. It is my purpose to take a brief general view of the trend of development, to deal with some particularity with an explosive of rather unique character with which I have had much experience, and incidentally to outline certain advantages and disadvantages of the new types.

The most striking feature among the changes occurring in the field is the almost omnipresence of nitrate of ammonia. Although a salt of a hypothetical metal it breaks down into a

<sup>1</sup> Presented at the 6th Annual Meeting of the American Institute of Chemical Engineers, The Chemists' Club, New York, December 10-13, 1913.

gaseous mixture containing a surplus of free oxygen and no solid residue whatever and, insofar, is therefore peculiarly suited to employment in explosives. Unfortunately it is very hygroscopic and of deplorably low specific gravity so that but a comparatively small weight can be packed into a given cavity. On the other hand, its adaptability, within the above limitations, is remarkably wide and we find it associated with almost every ingredient known to explosives manufacture, and especially with nitroglycerin. So wide is the present market for this material for use in explosives that practically the entire output of the gigantic Norwegian Atmospheric Nitrate works is now delivered in the form of nitrate of ammonia, and further important developments in the cheap manufacture of this important compound are to be looked for in the very near future.

Perchlorates, and especially perchlorate of ammonia, have

numerous advocates among the inventors, but so far do not appear to have entered the market to any very great extent. Perchlorate of ammonia is obviously, from its chemical formula ( $\text{NH}_4\text{ClO}_4$ ), well adapted to act as an explosive itself and at the same time provide three atoms of excess oxygen to combine with additional material. Aside from any other considerations, it possesses the serious defect of liberating considerable hydrochloric acid or a mixture of the same with chlorine. The use of certain powdered metals in the mixture serves very largely to eliminate both of the above gases.

A most profound impression has been made in the explosives trade of late years by the nitro derivatives of toluol, and especially by the various commercial mixtures of di- and trinitrotoluol now on the market. The cheddites (practically mixtures of the nitrotoluols with chlorate of soda and a vegetable oil, preferably castor oil) have achieved considerable well earned popularity, and the flood of current patent applications for explosives containing trinitrotoluol reminds one of nothing so much as of that which occurred some ten years ago for acetylene generators. Bearing in mind that trinitrotoluol possesses certain of the properties, so far as explosive effects go, of nitroglycerine itself; that it withstands water and is not affected by cold, and that it can be handled with absolute safety until blended with other materials that may increase its sensitiveness, it is not difficult to understand the enthusiasm with which it has been received by amateurs as well as by others in the explosives field. Aside from any admixture with other materials it forms, in the refined condition, an explosive of quite ideal properties for use in shells, torpedoes, mines and the like. And, notwithstanding its inert behavior, it can be depended on absolutely to explode completely when exposed, in a suitable physical condition, to detonation from an adequate primer. Several European governments are now making extensive use of this intensely explosive compound. Owing to the fact that its constitution ( $\text{C}_7\text{H}_5\text{N}_3\text{O}_6$ ) presents too little oxygen completely to combine with the carbon contents even to the monoxide form, the result of explosion is the formation of a cloud of carbon particles which will presumably have advantages in warfare, both through marking the position of a shell at the instant of explosion and in obscuring the enemy's vision.

The liquid nitrotoluols are also finding an important use in connection with nitroglycerine. They greatly lower the freezing point of the latter, contribute their quota to the explosive effect, and render the resulting explosive much safer than before.

In addition to the above compounds and many others (including the nitronaphthalenes, benzenes and xylois) the old stand-by, chlorate of potash, holds its own as a prime constituent of modern disruptive powders. It may be worth while to glance for a moment at the extraordinary thermo-chemistry of the chlorates and perchlorates, the same having a vital bearing on the matters of energy developed, sensitiveness and stability of certain explosive mixtures containing them.

Chlorate of potash disengages heat energy to the extent of 93,800 calories per kilogram molecule on formation from its elements, but potassium chloride disengages 105,700 calories, or 11,900 more than the chlorate. The addition of three atoms of oxygen to the chloride is accompanied by the absorption of energy to this latter extent, the formation reaction being endothermic. Perchlorate contains one-third as much oxygen again as chlorate, but, instead of the addition being accompanied by a further absorption of heat, there is actually a disengagement of energy, accompanying the entry of this lone atom, of far more (19,900 calories altogether) than the entire amount absorbed when the first three atoms were added. Chlorate stands ready

to fall to pieces on scant provocation and, in doing so, gives up not only three atoms of active oxygen to any combustible in the neighborhood, but 11,900 calories per kilo molecule as well. Perchlorate, on the other hand, in spite of its higher degree of oxygenation, requires more energy to drag it to pieces than does the chloride itself, and, in consequence, forms a less sensitive and less energetic constituent for an explosive than the less oxygenated chlorate.

In the light of the above, and especially in view of the fact that the besetting trouble with most modern chlorate explosives is lack rather than excess of sensitiveness, it will be seen that plain chlorate presents certain large advantages over perchlorate for many explosives. This will help to explain the fact that, although modern electrochemical methods enable the ready production of perchlorates, the latter have not, as stated above, so far become serious competitors in the field of commercial explosives.

To illustrate the remarkable extent to which the desensitizing of at least one chlorate explosive has been carried without destroying its practical usefulness I will now cite the case of an explosive developed by me some seven years ago which has been in somewhat wide-spread practical use since that time.

In manufacturing this powder 5 parts of paraffine wax are melted and 4 of ground sulfur and 22 of nitrate of soda stirred into it; the mixture is allowed to cool and is then grained. The resulting material is called "mineral base." In spite of containing an oxidizing agent and combustibles it is completely inexplosive technically. It is finished to explosive by dusting 8 parts (to the above 31 of base) of powdered chlorate of potash over the grains. The final material possesses a number of interesting features. Due to an extremely low speed of detonation it develops its power in a way peculiarly available for the requirements of many large applications such as heavy rock work, clearing land of stumps and the like; and, owing to the said low speed of detonation, its high effectiveness for these purposes, even compared with explosives possessing decidedly greater energy content, is quite surprising. Its insensitiveness is such that it withstands the impact of a steel tipped service rifle bullet fired from the regular service rifle with a standard charge behind it without response of any kind; although, due to its property of going out after being set fire to when the flame causing ignition is removed, it is possible that incipient ignition occurs during the passage of the bullet. If packed hard it is impossible to explode it by any means whatever. On the other hand, loaded loose, it is an absolutely sure fire with a No. 6 detonator even when unconfined, and, for work in earth, as in removing stumps, it is necessary to bear in mind that confinement may be negligible. When well confined in large shots in solid rock, and especially if detonated with a stick of dynamite, it will withstand any reasonable amount of packing and still give a sure fire. From its composition it will be obvious that it is non-freezing, and, indeed, owing to the paraffine wax incorporated in it becoming harder with increasing cold, it loses its porosity through being pressed into holes less readily cold than otherwise. With regard to stability, it withstands the International Stability Test ( $75^\circ\text{C}$ . for 48 hours) with indifference, whether with moisture added or not, and some millions of pounds have been used during the past seven years, and in some cases excesses over requirements have been stored by contractors in badly constructed magazines, occasionally for years, and there has never been any sign of heating or decomposition, incipient or otherwise.

The very low chlorate content and the fact that all the other materials are used in their crude commercial condition, together with the extremely simple process of manufacture, render the cost of this powder exceptionally low. It is known under the name of R. R. Virite. A blast containing 600 fifty pound cases was fired on the Canadian National Transcontinental Railway



work on the Quebec-New Brunswick border, near Notre Dame du Lac, some years ago, and the two largest blasts at Prince Rupert, the Pacific Coast terminal of the Grand Trunk Pacific, 3500 miles from Notre Dame du Lac, were also shot with it, the charges containing respectively, 1010 and 1000 fifty pound cases of the explosive. Aside from the technical importance of these blasts the spectacular effect is quite indescribable. To give an idea I may say that in the one of these shots that I witnessed the mass of broken rock that had mounted in the air about three seconds after explosion occurred, and which looked like nothing so much as a vast and spreading black tree, contained, to state it in units that will make it sound as impressive as possible, about 175,000,000 pounds. Reference to the efficiency of virite in agricultural work is contained in *Bulletin No. 134*, entitled "Land Clearing," issued from the University of Minnesota by Prof. A. J. McGuire, Superintendent of the North Central Experiment Station.

With reference to the property which this explosive, in common with very many others, has of being more difficult to explode as its porosity diminishes, I wish to point out a certain important corollary which exists in a case where the insensitiveness when closely packed reaches the point it does in a case such as the one under discussion. If compressed forcibly to a specific gravity of about 1.45 it has been found impossible to explode by any amount of detonation, no matter what the degree of confinement. This in spite of the fact that a certain small amount of local combustion occurs where the material is in direct contact with the detonator. The superficially paradoxical situation confronts us that the only condition in which the material can be exploded by hammering between hard surfaces is one in which it becomes insensitive to detonation from another explosive. By this is meant that, in order to cause explosion of the powder by hammering, it has to be packed to a maximum density before the pinching between hard surfaces necessary to cause explosion occurs. Of course what happens when the material is hammered on an anvil is that any excess over what can be pinched down to the thickness of thin paper between hammer and anvil is forced aside and only the trifling amount of powder actually so pinched goes off, and it has hitherto been found impossible by any degree of practicable impact to communicate explosion from the quantity so pinched to the rest of the mass of powder. The importance of this peculiarity in securing freedom from accidents in any case other than where the powder is exposed to detonation from another explosive will be obvious.

If we consider what is the fundamental difference between the blow of a hammer and that of a detonator we see at once why a mass of the explosive which refuses to transmit detonation, however powerful (within the enormous upper limit experimented with) when in a dense (non-porous) condition—why such material may be readily exploded when in a porous condition by a detonator although a blow from a hammer can have only a local effect. The point is that, in the former case, the blow is struck so quickly that the explosive is hammered between the products of explosion of the detonator and, if I may so express it, its own inertia, without having time for its porosity to be interfered with. The passage of a bullet exposes it to the same kind of a blow against its own inertia, but the swift bullet is so far inferior in speed to the velocity of the products of explosion of a detonator that it falls short, in the case of a powder of the class under discussion, of producing an explosion. There is also, of course, the essentially important feature, in the case of explosion by a detonator, of exposure to vastly greater heat than from the friction of a bullet or impact of a hammer.

The well compressed material behaves, as previously stated, in a completely inert fashion to attempts to detonate it, but mere crumbling restores it to the explosive condition. It would seem as though a technical division on the lines of classification according to safety might well be adopted to embrace explosives

that require outside detonation from another explosive in order to set them off.

I must not close without making reference to liquid oxygen as a constituent of explosives. Modern methods exist for producing this element in a state of high technical purity in the liquid form at a cost extremely low compared with its cost in the combined form in any of the chemicals employed in the explosives trade, so that completely smokeless and fumeless mixtures equal to 75 per cent dynamite can be made at a cost of about 2 cents per pound. As regards safety, explosives containing liquid oxygen stand in a class by themselves in one particular, *i. e.*, in the fact that, should a shot be missed for any reason, the charge presently becomes inexplodable through volatilization. Of course this is merely the merit which accompanies the greatest defect of these explosives. They must be used within a few minutes of being compounded. Nevertheless this is by no means the absolutely prohibitive feature that might be expected, owing to two considerations, one the numerous gigantic individual blasts that are necessary on certain heavy construction works (the time required for the charge to evaporate being comparatively long in such cases) and the other the fact that the addition of the liquid oxygen to the combustible portion of the charge may be made the last thing before firing. I am rather firmly of the opinion that in the heaviest construction works of the future, especially where the so-called "coyote" shooting can be employed, liquid oxygen will play an important part.

This paper is intended to deal with accomplished facts in explosives development and there is no occasion at present to do more than refer briefly to the hopes of the nitroglycerine manufacturers that in synthetically prepared glycol may be found the solution of their bondage to the fluctuation of the corn and cotton seed crops. The production of glycerine depends considerably on the abundance or otherwise of pork and of cotton seed oil and the former depends largely on the corn supply. The stearine candle industry, another feeder to the high explosives maker, is not in a healthy condition, and altogether the situation of the dynamite manufacturers is not so completely free from anxiety in the matter of their glycerine supply as they might wish.

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## EXPERIMENTS WITH SMALL ANIMALS AND CARBON MONOXIDE<sup>1</sup>

By GEORGE A. BURELL AND FRANK M. SEIDERT

The usefulness of small animals in detecting vitiated air in mines is well established. The Bureau of Mines and others have much information on this subject, but in order to make this paper brief, accounts of their practical use or of accidents because they have not been used will not be given here. Time can be devoted, if so desired, to this phase of the subject in the discussion.

The Bureau has experimented with most of the more common small animals, such as canaries, guinea pigs, rabbits, chickens, dogs, mice and pigeons, and finds that canaries or mice are the most suitable for the work. Of the two the Bureau finds canaries to be the most sensitive. They were used in England before their acceptance in this country, presumably in places on the continent also. Their usefulness in husbanding the resources of breathing apparatus is of great importance.

An additional reason for the use of canaries lies in the fact that they are generally easily obtainable, and become pets of the men who have them. If handled intelligently in rescue operations, they seldom die as a result of their exposure to carbon monoxide.

<sup>1</sup> Presented before the Coal Mining Institute of America, Pittsburgh, Pa., December 4 and 5, 1913. Published by permission of the Director of the Bureau of Mines.

In rather a brief manner, one of the objects of this paper is to give the results of experiments by the Bureau which have shown that they may be used repeatedly in rescue operations without danger of their being more susceptible to carbon monoxide poisoning after several or many exposures. This fact had not been determined experimentally hitherto, as far as the authors are aware. A second important point has to do with the relative behavior of men and small animals to carbon monoxide. Carbon monoxide was the gas experimented with because it is the constituent of after-damp most insidious in its action, most difficult to detect, and responsible for most of the deaths caused by mine explosions. Small animals, however, also feel distress sooner than men in atmospheres vitiated by other gases than carbon monoxide.

#### EFFECT OF REPEATED EXPOSURE TO CARBON MONOXIDE

Details of these experiments will be given later in a publication of the Bureau. They will only be outlined here. Canaries, mice and guinea pigs were repeatedly exposed to carbon monoxide under different conditions. In some experiments they were exposed to atmospheres that distress them in about two minutes. In the case of canaries 0.25 per cent was used in some experiments, and the animals were exposed 7 to 10 successive times. For instance, the animal was exposed to collapse, and then, when it had apparently recovered (7 to 12 minutes), it was exposed again and again, the object being to see if, after many exposures to a certain percentage of the gas, it would upon subsequent exposures show distress in a greater length of time, *i. e.*, become more or less acclimatized to the gas. No acclimatization effect was noticed. The same experiment was performed with mice and guinea pigs with the same result. Different percentages than 0.25 per cent were also used in the case of both canaries and mice. The experiments were also carried further to the extent that the same animals that had been exposed several or many times on one day were exposed several or many times the next day and on successive days.

Animals were also exposed to percentages that quickly distress them, and after the removal from the atmosphere and recovery were placed in atmospheres that ordinarily do not apparently affect fresh animals. This experiment was also reversed in the case that the animals were first placed in atmospheres that do not affect them, say 0.10 per cent in the case of canaries (for a long time, at least), and then they were exposed to atmospheres that ordinarily affect them quickly to see if results different from the ordinary could be obtained. In performing this work, the results of which can be briefly told, but which required considerable time for its performance, the conditions of recovery work with the aid of small animals was kept in view. In such work parties would usually advance until the animals showed distress. The animals would then in all probability be carried back to fresh air, and further advance, if such were made, would be accomplished with breathing apparatus. A general reconnaissance might be made with the animals to define the danger zone of the mine. In the latter event they might be exposed to proportions of carbon monoxide that would, in each case, cause collapse. Another possible contingency has to do with the use of the animals in a part of the mine where very small proportions of carbon monoxide exists, say 0.10 per cent, a proportion that does not seem to affect canaries or mice (as far as can be observed) in one or two hours' time, and then their use in a place where a larger percentage might be present. It is possible, too, that an animal which collapses at a certain place because of the proportion of carbon monoxide there, might, upon recovery, be used in an atmosphere containing a proportion that does not usually affect a fresh animal. Finally the same animal might be exposed over several successive days while a mine was being explored. It is believed that the experiments performed show that animals will not become acclimatized to carbon monoxide under the conditions surrounding recovery work in mines, and hence become less useful and even a source of danger. It might be mentioned

that this question has been raised several times in discussing the use of small animals for detecting after-damp in mines.

It should be mentioned that two Canadian investigators, G. G. Nasmith<sup>1</sup> and D. A. S. Graham, found that the animals finally become acclimatized by continued exposure, *i. e.*, if a guinea pig is exposed for days and weeks to small percentages it can finally stand exposures that would otherwise kill it, but our tests have shown that in the case of small animals which are quickly removed to fresh air (after distress is shown) and then exposed again for a reasonable number of times, this acclimatization effect is not apparent. The two methods of experimentation are not parallel. It is pertinent to add that the effect Nasmith and Graham observed in guinea pigs, an increase in the red-blood cells, has been observed in men working around blast furnaces. Blast-furnace gas contains a high percentage of carbon monoxide.

#### EFFECTS ON THE DIFFERENT ANIMALS OF THE SAME PROPORTIONS OF CARBON MONOXIDE

The Bureau has performed many experiments in order to draw some conclusions regarding the effect on different animals of the same species of a given proportion of carbon monoxide. It was found that in general a given proportion of carbon monoxide affected different animals of the same species in about the same length of time, at least as far as the application of the results to the practical use of the animals in mines is concerned, but that once in a while an animal might behave markedly differently from what is expected. This is more true of mice than of canaries, yet even in the case of the latter several of them should be taken with an exploration party.

#### THE RELATIVE EFFECT OF SMALL AMOUNTS OF CARBON MONOXIDE ON MEN AND SMALL ANIMALS

In reading over accounts of rescue and recovery work in mines, one is impressed with the fact that some users of small animals have not been entirely satisfied with the behavior of mice and birds (especially mice) in that men have apparently felt distress before the animals became affected. The Bureau, as the result of many experiments made to determine the resistance of small animals to carbon monoxide poisoning, believes it has the data at hand which explains partly this dissatisfaction.

It was found, for instance, that almost all of the animals tried do not show sufficient distress in one hour's time with 0.10 per cent of carbon monoxide to make them valuable for detecting this percentage of the gas. In some cases the length of exposure was extended to three hours without any pronounced effects being observed. In one case only was a canary affected in so short a time as 12 minutes by 0.10 per cent of carbon monoxide. With another bird and the same percentage of carbon monoxide, distress was scarcely observable in 3 hours. Only a disposition to remain quiet was observed. Eight different canaries were used and six different mice. Only one mouse out of many was slightly affected in so short a time as 30 minutes with 0.10 per cent, but it was not overcome in 4 hours. Neither were chickens nor pigeons visibly distressed. With 0.15 per cent both canaries and mice began to be affected. With 0.15 per cent carbon monoxide canaries showed distress in from 5 to 30 minutes. A mouse showed slight distress at the end of an hour. With 0.20 per cent, canaries responded in from 2 to 5 minutes except in one case (35 minutes). Three mice responded in 12 minutes, and a fourth in 46 minutes. No blood tests were made, the object being to determine the usefulness of the animals for mining work where their behavior as apparent to the eye is the only guide. Haldane states that 0.06 per cent carbon monoxide is sufficient to produce distinct symptoms in mice.<sup>2</sup> The authors of this paper do not hesitate to say that because of his greater experience in experi-

<sup>1</sup> "The Haematology of Carbon Monoxide Poisoning," *Journal of Physiology*, **25** (1906), Nos. 1 and 2, 32-52.

<sup>2</sup> "The Relation of the Action of Carbonic Oxide to Oxygen Tension," J. S. Haldane, *Journal of Physiology*, **18** (1895), 201-217.

menting with small animals Dr. Haldane might detect outward symptoms in a mouse that would escape the authors' attention. On the other hand, the authors have had greater experience than many of those who might use small animals in mines. Further, in the laboratory, observations are better made than in the mine where the light may be poor. Dr. Haldane made many experiments with himself as the subject in determining the effect of carbon monoxide on men.<sup>1</sup> He found that 0.12 per cent causes a mouse to sprawl in 11 minutes. Haldane felt a slight tendency to palpitation in 33 minutes. In 90 minutes he had distinct dimness of vision and hearing and a slight tendency to stagger, besides abnormal panting when he stopped the experiment long enough to run up and down stairs. In two hours' time vision and hearing became markedly impaired and there was some confusion of mind. When the mouse was finally removed from the cage it could not move about. After 18 minutes from the time of stopping, Haldane had a distinct throbbing headache which did not last long.

With 0.045 per cent of carbon monoxide Haldane did not notice any symptoms in the 4 hours that the experiment was carried on, but on running upstairs there was unusual panting, slight palpitation, etc. A mouse was not distinctly affected. In defining the minimum harmful or poisonous percentage of carbon monoxide, Haldane states that 0.05 per cent in pure air is just sufficient to produce in time very slight symptoms in man, and the same percentage produces very slight symptoms in mice. He states that 0.20 per cent is very dangerous to man. With 0.05 per cent and thereabouts Haldane finds that the gas finally begins to affect men and the outward signs appear in mice.

Haldane's observations on mice are not entirely in accord with those of the authors of this paper. The reasons are probably, as already stated, differences in observation. The authors are convinced from their experiments that in a mine with poor light, and perhaps only hurried examination of the animals, and by persons more or less inexperienced in the actions of the animals, mice and canaries will not usually show distress pronounced enough to give good warning with 0.10 per cent or less of carbon monoxide. Haldane's work shows that this percentage may finally affect men—a headache in 40 or 50 minutes perhaps, or slight tendency to palpitations in less time. This condition will be a considerable time removed from actual distress or unsteadiness of movement. At the end of 20 minutes one of the authors of this paper had only a slight headache when he exposed himself to 0.25 per cent carbon monoxide (in air); later, however, he became very ill. Canaries collapsed in just a few minutes.

In connection with the above laboratory experiments the authors have made observations regarding the use of small animals in mines. One instance is noteworthy, as follows:

A mine fire occurred recently and a sample of mine gas was obtained that contained the following constituents:

	Per cent
CO <sub>2</sub> .....	1.10
O <sub>2</sub> .....	18.61
CO.....	0.12
CH <sub>4</sub> .....	0.42
N <sub>2</sub> .....	79.75
Total.....	100.00

This sample was obtained in a place where exploration work was being conducted. Canaries carried with the party were not affected but two of the men finally complained of a bad headache. Later when they went to the surface they became ill. One was indisposed all evening.

These facts, although they appear damaging against the use of small animals for the purpose proposed, only militate in part against their usefulness. They still remain, in the authors' opinion, the best indicators of carbon monoxide that we

<sup>1</sup> "The Action of Carbon Monoxide on Man," J. S. Haldane, *Jour. of Physiology*, 18 (1895), 430-462.

have for exploring parties in mines. Canaries will give ample warning of percentages of carbon monoxide immediately dangerous to men. When the proportion of carbon monoxide is 0.15 per cent, canaries will show distress usually in from 5 to 12 minutes. With 0.20 per cent the distress is usually apparent in from 2 to 6 minutes. For distress to appear in men with these percentages requires much longer time, although in the case of some individuals the effects may, when they do disappear, last for hours. The authors have also determined this point experimentally, as have others. Men cannot stand the exposure to collapse from carbon monoxide like animals can. Canaries and mice after distress and collapse recover quickly if exposed to fresh air—only a matter of minutes usually. In the case of men exposed to collapse, recovery is often a matter of days.

In assigning reasons for the different effects produced on men and small animals by small quantities (say 0.10 per cent and under) of carbon monoxide, the authors of this paper would say that it is largely a question of observation. The blood of the animal is, of course, taking up the carbon monoxide, but only slowly and to the extent that even after a long time, one hour or more, the only effect observed in the animal may be a slight sluggishness or disinclination to move about. Men, on the other hand, especially when moving about or doing hard work, absorb much more oxygen and hence more carbon monoxide than when at rest, and may finally feel a slight or even a severe headache in the same gas mixture that is only slightly or not affecting the animals (as far as can be observed). The men may even finally become very sick. It is not believed that any pronounced acclimatization effect is produced in an animal on a short exposure which would account for the apparent resistance. It must be remembered that a man is in an excellent position to determine effects upon himself long before distress occurs, in the case of small percentages of carbon monoxide. Small animals may feel distress but not show it.

When the carbon monoxide content of an atmosphere is raised from 0.10 per cent to say 0.15 or 0.20 per cent, the susceptibility of a canary or mouse to the gas is markedly increased, as judged by the action of the animal; so much more so than in the case of men that a canary especially may show distress in 5 minutes, while a man may require 30 or more minutes. A man if he expose himself this long, however, may finally become very sick, and if for longer periods, may become dangerously so.

#### EFFECT OF CARBON MONOXIDE ON DIFFERENT MEN

The Bureau has compiled data from different sources to show the effects produced on different persons by carbon monoxide. The fact is clearly brought out that the gas may affect different persons in a different manner. Long-standing after-effects produced in people by severe poisoning, although apparently rare, are by no means unknown. It appears to be the evidence usually that recovery from exposure is complete but that in the case of some individuals long-standing after-effects may follow. These after-effects on different people cannot be connected absolutely with any degree of exposure, *i. e.*, one short exposure to large percentages, repeated exposures to large percentages as usually happens in the case of blast-furnace gas, or slow exposure to collapse with small percentages of the gas, as in the case of miners exposed to the smaller percentages that are found in mines following explosions. In the case of the same individual, the final blood saturation is what counts, of course. The point is that different people may withstand different degrees of blood saturation. In the case of blast-furnace men, the same men may be exposed to collapse or severe temporary sickness time and again. Usually, as far as can be observed from their behavior, they retain their normal condition, although, as has been pointed out by Thomas Oliver, severe after-effects may linger for two years.<sup>1</sup> This appears to be exceptional. An Illinois commission,

<sup>1</sup> Thomas Oliver, "Diseases of Occupation," p. 67.



appointed to inquire into conditions around steel plants, found it hard to separate effects on steel workers produced by bad living conditions and those produced on some of the men by carbon monoxide, although they were inclined to the view that carbon monoxide poisoning had considerable to do with the generally poor condition of some of the employees. The exact action of the gas in producing bad nervous disorders still remains somewhat obscure. Some do not believe the action so simple as to merely temporarily deprive the system of oxygen, although most of the good experimental evidence points to this view. An analogy has to do with men who work at high altitudes or suddenly ascend to extreme heights in balloons, where the oxygen tension is very low. Different individuals may also be affected differently at high altitudes. One must believe that in cases both of carbon monoxide poisoning and of oxygen deprivation by other causes, the idiosyncrasy of the individual plays an important part. Others have laid much stress on this point.

As regards acclimatization to the gas, it has been strikingly shown that guinea pigs may become immune. The compensation found in pigs has also been in part observed in men. The red-blood cells increase to compensate for those put out of action by the carbon monoxide. How long this may continue without pronounced distress on the part of men is important.

Repeated exposure to carbon monoxide may occur in the case of miners, in those who do the shot-firing. Blasting explosives always produce some carbon monoxide in coal mines. Men may return too quickly to the working face (before gases have disappeared), to examine their shot, and thus expose themselves to percentages, usually small, of the gas. Where large shots are fired, where the ventilation is poor, and where the working faces are too far ahead of the last breakthrough, contact by men with harmful percentages of carbon monoxide and other poisonous gases may follow. Miners at some mines frequently go home sick from powder smoke. The general effect of such exposure on them cannot be anything but bad.

In the conduct of exploration work, one sometimes hears it said that certain individuals of a party were able to withstand atmospheres that caused distress in other members of the same party. This may be true because some men are more affected than others by the same properties of the gas, but one or two other causes must be kept in mind. After-damp in different parts of a mine (in some places quite close together) will differ much in composition to the extent that at one place a very small and insignificant amount of carbon monoxide might be present, while at another place, close by, a harmful proportion might exist. One person of a party unknowingly might encounter the latter atmosphere while his comrades do not. Another reason usually less apparent to an exploring party has to do with the fact that the amount of carbon monoxide absorbed depends, of course, upon the air breathed. A man at rest may breathe 7 or 8 liters of air per minute. By even moderate exertion this can be increased to 3 or 4 times that quantity. It follows that if one or more members of an exploring party work harder than others they will become poisoned more quickly than the less active members.

#### SUMMARY

1. Small animals may be repeatedly used in exploration work without becoming less useful as indicators of carbon monoxide.
2. Of the more common small animals, canaries are best adapted for exploration work.
3. Men may feel distress, especially if they work hard, in the presence of small proportions of carbon monoxide (0.10 per cent or under), when animals at rest in their cages do not distinctly show it.
4. It is occasionally found that different animals of the same species may be differently affected by the same proportion of carbon monoxide; hence more than one animal should be used at a time.

The conclusions given are drawn from the authors' work on small animals and men, from J. S. Haldane's work on small animals and men, from the accounts of exploration work of dissatisfied users of small animals (especially mice), and some miscellaneous observations by the author on the use of small animals and general effects of carbon monoxide.

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#### CHEMICAL INDUSTRIES AND SCHOOLS

By DANIEL M. GROSS

The writer through an address on the subject "What's the Matter with the American Chemist?" which appeared in *This Journal*, 5, 692, has been favored with the views and opinions of various correspondents. These communications were extremely diverse as to the reason why we cannot compete with foreign chemical producers, but all agree upon the one fact that Germany leads the world and controls the markets in chemical products.

The writer mentioned the chaotic condition of the dyestuff industry because at the time much newspaper space was being devoted to the agitation in that quarter, and, taking the situation in its entirety, this phase of the question is only one small link in the chain of chemical products.

The address evidently touched a responsive chord and caused some serious thinking and has brought to light some facts bearing on this subject which have hitherto remained obscured or vague. One correspondent in expressing his views on the question "Why cannot we make chemicals to supply our needs without importing them?" tersely answers "We can but we won't." The truth of this statement is greater than it appears at the first glance and seems to answer the question most effectively, but at the same time there pops up another "Why?"

In this as in all subjects much remains hidden that bears largely upon existing conditions and each influence is effective to a greater or less degree. It is the intention to discuss those influences which, according to the opinions of various interested correspondents, have been responsible for this country being left behind in the great race for supremacy in this industry.

The issue at stake, however, is not the reasons or results but the remedy. This means the hard cash of a prosperous industry, a commercial proposition. It is well to remember that every new industry created means just so many more mouths fed, so many more families maintained and so many more citizens preserved to usefulness and productiveness.

Closing our eyes to an unpleasant truth does not alter the situation and even though it hurts to admit it we must acknowledge that we have learned only the trade of producing chemical products instead of the science of chemistry. We had the same opportunities and greater advantages than Germany for the exploitation of the chemical industry but allowed them to slip through our hands and be eagerly grasped by the foreigner. In the early seventies, Germany was far below England and France in manufacturing, invention and foreign commerce. Overburdened with our productive lands and our natural wealths of raw materials, we have never been forced into the great fight for existence and many of our natural resources have passed from our control or remained undeveloped.

To speak of the chemical industry and not to mention the German syndicates would be omitting, perhaps, the main factor in the case. As every one knows, Germany possesses, to-day, the best developed chemical industry in the world and dominates the trade the world over. This syndicate of which we hear so much is something real and with enormous powers which it uses with a high hand. We have nothing to compare with it in our own land and its power is so great and so effectively does it control and regulate the market, that it can dump its supplies where it pleases and at prices to suit itself.

To this syndicate the German Government extends a helping hand at all times. It is Germany, first, last and all the time, and against the world. In the potash case a few years ago there was an actual partnership with the government to regulate the price of the potash and together they control the supply of the world.

To what extent the individuality of the chemist contributes toward the general situation is to be judged by the reader. Foreign chemists are satisfied with a small salary—*here*, three times as much pay is demanded. Graduates are glad to seize the opportunity to get into a factory at little compensation to get a start and for the practical knowledge they will acquire. This presents a phase rather unfamiliar to our general views and shows they have either a belief in themselves and their future or a willingness to sacrifice themselves for their love of profession.

If a graduate is satisfied to work for a small sum, eager for a chance to do great work at a personal sacrifice, it certainly shows a high degree of patriotism or an intense love of profession. Ambition will generally make good in any capacity and prove its worth. While the wages paid abroad are very much lower, this condition cannot have much bearing, when the different standards of living and relative costs of same are impartially considered.

Germany is spending enormous amounts each year for its chemical development through its universities in which the instructors and chemical factories cooperate with very successful results. An individual or manufacturer up against a difficult problem has at call the finest advisory talent available as well as adequately equipped laboratories at his disposal. When such authorities as Prof. R. K. Duncan and his associates are striving their utmost to bring about a similar condition, practically absent in this country, it is most apparent that this spirit of cooperation has a high potential value. That there is a lack of such cooperation as exists abroad between the manufacturer and the chemist and also between the educational, financial and commercial interests, all will admit, but why should it continue if such cooperation is to the advantage of all concerned.

The writer has knowledge of cases where firms refused to take advantage of new processes devised by interested employees to reduce costs and improve the output. Superintendents resented any suggestions except those emanating from themselves and looked upon such as a reflection upon their abilities. Instances of this nature are by no means rare and especially a few years back when "ignorance was bliss," this phase of "destructive conservatism" may have contributed its share towards placing the chemical industry in its present state. Such a spirit certainly does not promote the efficiency and low manufacturing costs which are essential in industrial progress. The

mental attitude of the worker is as important as scientific management and how much influence such incidents as the above have had upon the industry collectively depends upon the personal opinion of the reader.

Within the confines of Germany or France there is no such thing as a played-out farm. Land has been cultivated continuously year in and year out and to-day still shows a high degree of productiveness due to scientific application of fertilizers, which we are just beginning to get acquainted with. With the aid of the chemist, German farms are raising beets for sugar in competition with cane sugar and are producing beet sugar to the tune of 100 million dollars a year. Instead of sending their money out of the country for something they cannot produce, they keep it at home by discovering some substitute for the desired product. Again, the United States imports creosote for various purposes by the shiploads, produced from German coke ovens and permits the same by-product to go to waste at our own ovens. These two examples serve to show how we neglect our own resources and are simply a few out of many illustrations. It is not to be expected that we should appropriate all the means by which Germany has reached her present position. Times and conditions are constantly changing and the methods of twenty or thirty years ago could not be used to-day, but we can utilize those aids which our common sense tells us would be to our benefit and advantage.

We can develop our natural resources and make them productive. We can foster an intelligent effort to benefit and apply to industrial uses the energy and products of the individual investigator. We can establish laboratories where the problems of the manufacturer as well as the individual can be worked out. There can be cooperation between our industries and institutions of learning.

Let there be a campaign of education and enlightenment. It is surprising how little is known on this subject. Many persons well informed generally have but the slightest knowledge of existing conditions and even within the profession there is not the familiarity one would expect. We can look for no legislative assistance until the public is educated and as long as the truth is withheld and the gravity of the question is not impressed as a matter of public concern and welfare, there will be no progress.

Looking the situation squarely in the face and casting aside all prejudice any person intelligent and well informed can see what our future will be. To be honest in one's convictions does not mean pessimism or calamity howling. Let us learn the truth, rectify our mistakes and build anew. A campaign of education once inaugurated cannot fail to bear fruit. Will American industry heed the lesson contained in rich England's industrial eclipse, in poor Germany's steady rise?

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## VENTILATION SYMPOSIUM

The New York Section of the American Chemical Society held a Symposium on Ventilation at The Chemists' Club, November 7, 1913. The various phases of this vital subject were discussed by qualified experts and their addresses are printed in full below. [EDITOR.]

### PHYSIOLOGICAL PROBLEMS OF VENTILATION

By FREDERIC S. LEE<sup>1</sup>

Man is intimately dependent upon his environment. In civilization he lives under artificial conditions, and it is, therefore, necessary to employ artificial means in order to adapt his environment to his physiological needs. The air surrounding his body is one of his indispensable environmental factors, and

when it is confined between walls the process of ventilation is required to keep the air in such condition that he is able to live within it in a physiological state. It cannot be too strongly emphasized that the problem of ventilation is fundamentally a physiological problem, and it must vary from time to time as the knowledge of man's physiological requirements becomes more exact. We know now much more fully than we knew a few years ago what qualities the air that he is to breathe ought to possess, and a few years hence our knowledge will doubtless be still more full. A few years ago ventilation was supposed to be a matter of maintaining the proper chemical purity of respirable air. It was only natural to draw this inference from the known fact that respiration renders the air chemically impure. The chemical compositions of inspired air and expired air are as follows:

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	Inspired	Expired
Oxygen.....	20.94	16.4
Carbon dioxide.....	0.03	4.1
Nitrogen.....	78.09	78.09
Argon.....	0.94	0.94
Helium, krypton, neon, xenon, etc.....	Traces	Traces

In considering the chemical vitiation of air by respiration it is obvious that the inert nitrogen, argon, helium, etc., may be neglected, and that attention should be focused upon the oxygen and the carbon dioxide. The necessity of oxygen in respiration has long been recognized, and it was long believed that its diminution, especially in the more extreme conditions, was a factor to be considered in ventilation. Against carbon dioxide the case seemed even stronger. It is increased more than one hundred times by the act of breathing; it was known to be poisonous to man; and its elimination was long believed to be the all-important requisite in adequate ventilation. The object of ventilation was thus to remove chemically impure air and introduce chemically pure air and plenty of it.

In recent years with the extension of human and animal experimentation the aspect of the subject has quite changed. It has now been shown that the oxygen of respirable air may be reduced to less than 17 per cent before its diminution becomes harmful. This proportion is too small even to support combustion. Hill says of a group of his students whom he confined in a small air-tight room: "We have watched them trying to light a cigarette (to relieve the monotony of the experiment) and, puzzled by their matches going out, borrowing others, only in vain. They had not sensed the percentage of the diminution of oxygen, which fell below seventeen." Except in extreme experimental conditions the amount of oxygen in crowded assemblies never falls below one-twentieth of its usual amount, *i. e.*, rarely below 20 per cent. Oxygen will, therefore, take care of itself and may probably be wholly left out of consideration in ventilating systems.

With the poisonous carbon dioxide, too, the case now seems not so very different. Within man's body carbon dioxide plays essential rôles. It is the stimulant which excites the nervous center of our respiratory mechanism and maintains its regular action, and a similar hormone influence has been recognized in other bodily functions. Moreover, the poisonous properties of carbon dioxide when in air have been exaggerated. Experimentation indicates that it does not become harmful to man until it accumulates to about one per cent or nearly forty times its usual amount. In crowded rooms it very rarely reaches even 0.4 per cent, or ten times its usual proportion in pure air and only one-quarter of its harmful amount. Like oxygen, therefore, it would appear that carbon dioxide may probably be eliminated from the problem of ventilation except under the most extreme and unusual conditions. It is still customary to use as the standard of suitable ventilation the amount of carbon dioxide permissible in the air of rooms. In the United States we are still very deficient in ventilation laws, but in England specific laws fix the quantity of this gas which may be permitted in the work rooms of certain industries. In view of the present status of physiological knowledge it would appear that some other standard than that of a fixed amount of carbon dioxide should be established.

Notwithstanding these recent changes in our ideas of the relation of oxygen and carbon dioxide to ventilation, I am not prepared to say without reservation that the continued exposure of an individual day after day and week after week to even a moderately diminished quantity of oxygen and a moderately increased quantity of carbon dioxide would be wholly without harm. But I am led to this reservation not by any existing positive physiological knowledge, but rather by the necessity of maintaining an open mind receptive to future possible discoveries—a mental attitude which ought always to characterize men of science.

There has long existed a belief, and even among scientific men, that expired air contains a peculiar organic and volatile constituent, probably of protein nature, which is toxic to human beings and other animals. Various attempts have been made to support this idea experimentally. The most of these experiments have consisted in condensing expired air and then injecting it into animals. Some of these experiments have seemed to result positively. The latest of these were performed by Rosenau and Amoss, in 1911, and the positive result was the production of an anaphylactic condition in a certain proportion of the experimental animals. One by one these successive supposed positive results have been balanced by equally significant negative results and have been explained otherwise than as indicative of the existence of the hypothetical substance; and now in this city Weisman and Lucas independently have repeated and extended the work of Rosenau and Amoss and have not been able to confirm their findings. In the light of present evidence, therefore, we cannot accept the belief that expired air contains an organic poison. Furthermore, the odor of air vitiated by human beings is no index of the presence of harmful ingredients.

It is pertinent here to refer to the case of ozone. Its powerful oxidizing properties and its intemperate advocacy by enthusiastic but unscientific persons have caused it to be hailed popularly as highly beneficial to the human body, not only in ordinary respiration but in the purification of the air of living rooms, and in the destruction of bacteria and other organic matter. In many offices and homes we find various forms of ozone machines, busily at work discharging into the atmosphere their peculiarly odoriferous product. Very recent investigations seem to make it clear that the supposed beneficial powers of ozone as a home companion are creations of the imagination. Two groups of American investigators, Jordan and Carlson, in Chicago, and Sawyer, Beckwith and Skolfield, in Berkeley, have independently carried out each a series of careful experiments<sup>1</sup> on the action of ozone on bacteria, animals and human beings. They find that ozone will indeed kill bacteria exposed in a room, but only when in such concentration that it will kill guinea pigs first. "There is no evidence for supposing that a quantity of ozone that can be tolerated by man has the least germicidal action." When present in any considerable quantity in the air ozone is irritating and probably corrosive to the lining membrane of the air passages of the nose, throat and lungs, causing the blood vessels of this membrane to be excessively dilated and to present the customary symptoms of "sore throat." It causes headache and drowsiness. The heart, at first accelerated, is later slowed and weakened, and the pressure of the blood in the arteries is unduly lowered. The case for ozone thus seems to narrow down to a supposed beneficial action in destroying or modifying unpleasant odors in the air of a room. When in not too great concentration such odors are, it is true, overcome, though it is quite probable that their disappearance is due, not to an actual destruction of the odoriferous substance, but partly to a replacement of the disagreeable odor by the odor of ozone and partly to fatigue or anesthesia of the olfactory membrane of the nose. It is very questionable whether this is wise, and Jordan and Carlson well say: "It seems to us that this is wrong in principle, and that ozone is being used and will be used as a crutch to bolster up poor ventilating systems. Ozone does not make pure air any more than strong spices make pure food." It thus seems probable that ozone as an adjunct to ventilation is destined to pass into oblivion.

Bacteria also may probably be eliminated as a factor to be considered in ordinary ventilation, for the idea is gradually making its way that the germs of infectious diseases are conveyed to the unfortunate individual almost wholly through some form of physical contact and that aerial infection occurs with extreme rarity. In exceptional cases air may be rendered un-

<sup>1</sup> See also *THIS JOURNAL*, 6, 882.



wholesome by the presence of poisonous gases. Instances of this are the leakage of illuminating gas from defective pipes and the production of poisonous fumes in certain industrial procedures. But it is now clear that sewer gas may be eliminated as a factor in our dangerous environment, for none of its gaseous constituents is markedly toxic and its bacterial content is so slight as to be negligible.

While it has thus been shown that it is not the chemical features of air and their relation to man which supply the physiological basis for the problem of ordinary ventilation, research has at the same time been demonstrating that two of the air's physical features appear to be the decisive factors. This idea seems to have been first suggested thirty years ago by Hermanns, and it has since constantly found increasing experimental support. Hence, in considering ventilation from the latest standpoint, we are obliged to turn from chemistry to physics. At the same time we turn also from the lungs to the skin. The physiological problems of ordinary ventilation have ceased to be chemical and pulmonary, and have become physical and cutaneous.

The average adult human body produces within itself and gives off to its environment during twenty-four hours, when at rest, 2400 calories of heat, and when engaged in vigorous physical labor more than twice this amount. Fully 95 per cent of this heat leaves the human furnace through the skin, partly by radiation and conduction, and partly by the evaporation of the water of perspiration. This loss cannot be regarded as one of nature's errors; on the contrary it is a physiological provision, carefully controlled by the nervous system, for the good of the organism. If this dismissal of heat from the body be prevented, heat will accumulate within—for its production never ceases throughout life—and deplorable consequences will follow. The bodily temperature will rise above the normal, and a febrile condition will result. There will be disturbances of metabolism, with the probable accumulation of abnormal and deleterious metabolic products; working power will be lessened; fatigue will come on early; and ultimately in extreme cases all the untoward phenomena of heat stroke will occur.

The normal loss of heat or, as the Germans call it, the "unwarming" of the body, may be interfered with by making the surrounding air too warm, thus preventing radiation and conduction; or by making the air too moist, thus preventing the evaporation of sweat; or most effectually by blocking both of these channels. This last-mentioned procedure is that which happens to human beings confined in improperly ventilated rooms. From their bodies the temperature of the air rises and the humidity of the air increases. As these events happen each body finds it not so easy as at first to rid itself of its superfluous heat, and this becomes increasingly more difficult. Heat-laden blood must be sent in larger quantity to dilated cutaneous arteries, flushing and warming the skin; sweat glands must be stimulated to visible activity; breathing must be deepened; and every method of which the body is physiologically capable is unconsciously brought into action to protect it. At first the sensations are merely those of general uneasiness, manifesting itself in restlessness; then progressively appear sleepiness, an oppressive sense of heat, headache, thirst, and still more severe sensations which, if relief is not obtained, may give place to the delirium of the Black Hole of Calcutta or the prison at Austerlitz—these sensations keeping pace with the development of the fever within and the other pathological events accompanying it.

Much experimentation has shown that these evil results of confinement in improperly ventilated rooms are caused not by the presence of toxic products of respiration, but by the heat and the humidity combined. Paul found that with human beings enclosed in a hot and humid experimental chamber the unpleasant symptoms began to appear within a few minutes

and before there was time for the accumulation of supposed poisonous gases. When the air of the chamber was put into motion the temperature of the skin fell, the unpleasant symptoms disappeared very quickly, and the subject felt as if fresh air had been supplied. When the subject had been confined for a considerable time and the symptoms had become well developed, the breathing of pure air through a tube passing from the subject's face through the wall of the chamber to the outside brought no relief. When, on the other hand, an outsider with his body surrounded by fresh air breathed from a tube, the vitiated air of the chamber, no unpleasant symptoms appeared. Such facts make it clear that the symptoms are due to the action of the vitiated air, not on the lungs but on the skin. In one of Benedict's experiments a subject was confined for three days in a respiration calorimeter. During the second day the ventilation of the calorimeter was cut down so that the products of respiration were allowed to accumulate. During nearly the whole of this period of twenty-four hours carbon dioxide was present in a quantity averaging 2.2 per cent, or more than seventy times the usual amount. The humidity ranged between 54 and 66 per cent, while the temperature remained practically constant at the comfortable level of 20° C., or 68° F. The subject possessed his usual good health and on that experimental day was said to be "in unusually good spirits." Hill confined eight persons in a small, air-tight experimental chamber, containing approximately only three cubic meters of air. The oxygen fell from 20 to between 16 and 17 per cent, and the carbon dioxide increased from 0.04 to between 3 and 4 per cent, or nearly one hundred times its usual amount. The symptoms of the action of vitiated air soon appeared. Then three electric fans attached to the ceiling were started and, although the temperature of the air was between 80° and 85° F. and it was very moist, the simple movement of this wet, hot, stale air brought complete relief, for the simple reason that it whirled away the still hotter stationary air from the surface of the bodies and allowed them still to eliminate their internal heat.

These experiments and many others have proved beyond question that the chemical purity of air vitiated by the presence of human beings is a factor of minor importance in ventilation, and that the qualities to be avoided are an elevated temperature and an elevated amount of moisture. In our American cities we know too well that the chief danger of our torrid summer days is not the heat alone, but the combined heat and humidity; but few persons realize that it is precisely the same factors that are responsible at all seasons for the evil effects of the confined air of rooms. There is no doubt that the air of our American living rooms and many schoolrooms and other assembly chambers is kept too warm. A temperature of 70° F. is commonly recommended for living rooms, but a lower temperature with a moderate humidity is more healthful. The British authorities advise temperatures reaching as low as 60° F. Acclimatization undoubtedly has much to do with the matter.

No fixed standard percentage of humidity can be set, since the percentage of humidity is so closely related to temperature. Thus 100 per cent of humidity in air of 65° is equivalent to only 58 per cent at 75° and 33 per cent at 85°. A humidity of 60 per cent with air of 68° F. is rational.

If any single standard is to be chosen as the standard of healthful air, it is probably the temperature of the air as indicated by the wet-bulb thermometer, for this is a measure of heat and humidity combined. The British authorities are very positive about this. Thus, Haldane summarizes his observations in these words:

"These experiments proved that in very warm air it is the temperature indicated by the wet-bulb thermometer . . . . . which determines the ill-effects produced. With a wet-bulb temperature exceeding 88° to 90° F. [= 31° to 32° C.] in fairly still air the body temperature begins to rise, even in the case

of persons stripped to the waist and doing no work; and when once started this rise continues until symptoms of heat stroke arise, unless the person leaves the warm air. In the case of persons doing muscular work, the rise of body temperature is much more rapid and begins at a much lower wet-bulb temperature. It will, for instance, begin (in persons stripped to the waist) at a wet-bulb temperature of about  $80^{\circ}\text{F.}$  [ $= 26.7^{\circ}\text{C.}$ ] in still air with moderately hard muscular work, so that hard and continuous work is impracticable at wet-bulb temperatures of over  $80^{\circ}$  in still air. There is no doubt that when ordinary clothes are worn, serious rise of body temperature occurs at a still lower wet-bulb temperature. Soldiers marching in uniform are, for instance, liable to heat stroke at wet-bulb temperatures of under  $70^{\circ}\text{F.}$  [ $= 21^{\circ}\text{C.}$ ]."

Thus, while the problem of ventilation seems clearly to resolve itself into the problem of supplying to the individual moving air of such a temperature and such a content in aqueous vapor as to enable him to maintain his body in its best physiological condition, there still remain many physiological problems related to ventilation which press for solution. At what temperatures and what degrees of moisture do the really evil effects of bad air begin to appear? In what ways other than the rise of bodily temperature and the obvious symptoms do these evil effects manifest themselves? Here there are many possibilities: alterations of respiratory exchange, of relations of the oxygen to the haemoglobin of the blood, of the action of the heart, of the pressure of the blood in the arteries, of the course of fatigue, of the working power of the brain. It must be believed that the normal course of the body's metabolism is altered, but no one knows with any degree of exactness what the alterations are. Do a high temperature and a high humidity bear any relation to bacterial infection? What are the differences between temporary and prolonged exposure to these unfavorable conditions? Most of the experiments heretofore conducted have been of short duration, and few have extended for so long a period as even a whole working day. Still fewer have related to the exposure, day after day, for weeks or months, to an atmosphere that is only slightly unfavorable; yet it is probable that the evil effects of such an environment are cumulative. How are the effects of a high temperature and a high humidity altered by performing physical or mental work? At what temperatures and humidities can physical work and can mental work best be performed—in other words, under what conditions of ventilation can the highest physiological efficiency of the individual be secured? Ought these conditions to be varied, and if so in what way, according to the occupation of the individual concerned? Should, for example, the home, the schoolroom, the hospital, and the work shop have each its own ventilation standard and in what terms should these standards be expressed? These are some of the physiological questions to be answered by the investigation of the future. What we already know about ventilation and what we hope to know in the future, combine to make it clear, I trust, that, as was stated in my introduction, the problem of ventilation is fundamentally a physiological problem.

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## MECHANICAL PROBLEMS OF VENTILATION

By D. D. KIMBALL

It is not my understanding that the subject assigned me refers to the details of the problem of working out a design for the ventilation of any building for any use, for such problems have become those of details only.

So far as this subject refers to the present wide-spread atmosphere of investigation into the general problem of ventilation it might almost be said that there are no mechanical problems unsolved in the field of ventilation; which is to say, the engineer

can provide any chemical or physical condition of the atmosphere of an enclosed space which may be required. The composition of the air may be maintained with any reasonable proportions of oxygen and  $\text{CO}_2$  (and ozone too, if desired) and the air may be kept freer of dust and bacteria than the outside air. It may be maintained at any temperature or any degree of relative humidity, and it may be given any degree of movement or diffusion desired. Odors and dust of any kind and of any amount can be removed.

These are matters fully understood by the engineer, and practice and formulae are at hand for guidance along correct lines.

The chemical and physical properties of the air may be varied at will and within short periods of time. And all of this may be accomplished by the artificial ventilating system. It cannot be accomplished by natural ventilation.

But nevertheless, someone will rise to insist that these things are not accomplished and that, therefore, these statements must be those of theory and not those of accomplished fact. And on the surface it appears as though such a person would not be far from right.

Therefore, let us briefly consider the reason or reasons. It will not be contended that there are not a great many ventilating systems in use which are justly the subject of criticism, even serious criticism, nor that there are relatively few systems in use for which entire satisfaction may be claimed.

But again, let it be stated that this condition results, not because of the mechanical problems involved but for other reasons, serious, and fundamental.

There is now no agreement as to which constitutes proper ventilation. Information is seriously lacking as to both the chemical and physical properties of the air which are most desirable. There are many chemical and physical phases of this problem which are of undoubted importance, such as oxygen, carbon dioxide, ozone, temperature, humidity, air movement, dust and bacteria, but in the case of no one of these elements is there entire accord among the Physiologists or medical men as to the effect of different conditions, except in so far as the trend of recent opinion seems to indicate that the physical, rather than the chemical, conditions of the air are of the greater importance, which is a reversal of earlier opinions. That is, temperature, humidity and movement of the air, and its freedom from dust, bacteria and odor are the first essentials of ventilation. Therefore, let the physiologist and medical men determine, by a continuance of the splendid studies and experimentation now going on, what are the most desirable atmospheric conditions. The engineer may then be counted upon to provide such conditions.

But decisions on these important matters must be well founded and may not be based upon insufficient investigations and inconclusive tests as have been so many of the recently announced views as, for instance, the oft reiterated pronouncements in favor of window ventilation. In the tests of this important phase of the ventilation problem, as recorded to date, the subjects have been in small classes under the care of specially selected teachers and nurses, with special diets, short study periods, exercise and rest periods, investigations and instructions regarding home conditions and with other details, all at variance with regular school practices, all of which doubtless materially affect the result, and yet the entire credit is given to the effect of the window ventilation. No consideration is given to the fact that proper window ventilation may be had upon but one or two sides of the building, and then only on the sides of the building which are favorably exposed, nor is any mention made of the enormous increase in the cost of maintaining the school system if such a system of school administration were applied to an entire city, such as New York.

In this reference to window, or natural, ventilation there is no intention to decry its use within proper limitations, nor as

an adjunct to the artificial ventilation system, which leads to the remark that a properly designed system of ventilation is not put "out of balance" by the opening of a window, the popular impression to the contrary notwithstanding.

Therefore, let the physiologists and medical men but come to an agreement as to the optimum atmospheric conditions and the engineer may be depended upon to produce just those conditions, IF, and herein lies the real problem of mechanical ventilation from the standpoint of the engineer, IF but a reasonable appropriation is made for the design and installation of the heating and ventilating system, and for its operation.

In the first place, not more than one plant in ten is designed, or laid out, by a consulting engineer. There may be, unfortunately, some practising engineers incapable of designing a system to meet modern requirements, but there are plenty of competent engineers. If a continuance of the unfortunate experiences of the past is to be avoided the owner must be made to realize that the design of a heating and ventilating system is no part of a plumber's work or an architect's work or training, for unfortunately some architects do not yet realize this fact and many architects prefer to entrust the design of the heating and ventilating plant to a friendly and willing contractor rather than to themselves pay the engineer's fee or to ask the owner to pay it. Result—the contractor lays out the work for his own benefit, is indeed glad to do so for the advantage which he may thus obtain over other bidders, the owner is without the expert services which he should have, and in the end he pays much more than enough extra for his plant and its operation than would have been required to pay directly for engineering services.

It is this class of engineering, also, which produces the most failures in ventilation work, the blame for which the engineer carries.

The cost of the best engineering services for the design and supervision of the heating and ventilating plant will vary from one-half to three-quarters of one per cent of the cost of the building.

A first-class engineer will produce savings in cost of installation and operation vastly exceeding this, and yet, but relatively few owners avail themselves of such services, while the wall against the inefficiency of the ventilating system goes on.

In the second place, in the case of nearly every building, the appropriation for the installation of the heating and ventilating system is reduced to the very minimum. Take, for instance, a school building. Usually a certain amount is appropriated for the building, then the committee selects its architect. If by competition, each architect strives to outdo the others in the size or ornamentation of the building which he offers to build for the amount appropriated. In any case the architect is usually confronted with the requirements of the committee, which requirements are from ten to twenty-five per cent in excess of what may be reasonably expected for the sum appropriated. And then begins the process of trimming, and the heating and ventilating plant, being the biggest single item of equipment, invariably comes in for the most attention and with the worst results. And this, too, despite the fact that the ventilating plant is really the lungs of the building and counts most for the comfort and efficiency of the building and its occupants. But, of course, there must be so many rooms, just so many gargoyles, and just so much marble. For these things are seen and read of all men. And thus the committee can point with pride to the size and beauty of its building and compare it with what a neighboring city secured for a similar sum.

Only recently an instance occurred where an expenditure of \$1,000 additional in the installation of the ventilating plant would have saved twice this sum in the annual operating costs but this could not be permitted because the money was needed by the architect for additional space in, or ornamentation of, the building.

The air washer, a most desirable adjunct to the school ventilating system, desirable because it eliminates dust, bacteria and odors and makes possible any degree of humidification, costing but approximately five per cent of the cost of the heating and ventilating plant, is rarely found in newly built school buildings, and solely because the school, or building, committee does not provide the means, or the architect, being forced to satisfy the committee as to the size or appearance of the building, cannot spare the money.

One of the most frequent complaints offered against the artificial ventilating system is that air of the same temperature is supplied to all of the rooms of the building, regardless of their exposure to sun and wind. Often a room on the sunny sheltered side of a building should have its entering air supplied at a temperature of from five to ten degrees less than the temperature of the air entering a room on the side of the building which is in the shade and exposed to a severe wind. But the common ventilating duct supplies the same air at the same temperature to all rooms. And this system is usually enforced because an extra expenditure of two to four per cent of the cost of the heating and ventilating system may not be permitted for the installation of a double duct system or an individual duct system, by means of which the temperature of the air may be regulated for each room according to its needs.

In the single, or common, duct system one duct leaves the heating chamber and branches to the vertical flue to each room. The double duct system has a second duct, carrying cooler air, directly under the above mentioned duct, also branching to the vertical flue to each room. Mixing dampers are provided at the base of each flue by means of which the mixture of warm and cool air entering the flue, and thus the room, is regulated by a thermostat in the room, according to its individual needs. In the case of the individual duct system, the most desirable but the most expensive, the duct for each room is carried back separately from the base of the flue to the heating chamber, which is, in this case, divided into upper and lower chambers, the air in the upper chamber having passed through all of the heating coils, and the air in the lower chamber having passed through but a portion of the heating coils. Connections are made from both chambers to each individual duct, with dampers in both connections arranged to operate in conjunction with each other, as controlled by the thermostat in the room, thus giving to each room air of a temperature suited to its needs, and without reference to the needs of any other room, either as to temperature or volume.

In the third place the difficulty of obtaining sufficient space for the installation of necessary apparatus and in obtaining suitable locations for ducts, flues, air openings, heating units and other details of the plant, places serious limitations upon the efficiency of the ventilating system, for diffusion of air and the resulting air movement are most important. The co-operation of the owner, architect and engineer are essential to the best results in this matter.

A further problem has to do with the standard of the janitorial service usually found in charge of the operation of heating and ventilating plants. Many well installed plants are rendered wholly inefficient by unskilled attention, and this despite the fact that the employment of a better class of operating engineers would result in a fuel saving more than sufficient to cover the extra cost of first-class and experienced men.

What has been said of the ventilation of schools applies with



equal force to hospitals, auditoriums, stores, factories and all other types of buildings.

In conclusion be it said that given authoritative standards, the employment of capable consulting engineers, a proper appropriation for the installation of the heating and ventilating system, a reasonable freedom to the engineer in the working out and in the application of his design, and skillful operation, and the engineer's problems in mechanical ventilation will have been overcome.

Without the consummation of these ends the splendid efforts now being made to solve the chemical, physical, physiological, psychological, efficiency and comfort problems of ventilation will have been wasted.

15 WEST 38TH STREET, NEW YORK CITY

## INVESTIGATION OF SCHOOL AIR IN NEW YORK CITY

By CHARLES BASEERVILLE

The Public School System of Greater New York has to do with over 700,000 children requiring the services of about 18,000 teachers with an annual expenditure of approximately \$40,000,000. The Board of Estimate and Apportionment approves all appropriations, which to be available must subsequently be passed upon by the Board of Aldermen. A special Committee on School Inquiry was appointed by the Board of Estimate and Apportionment to look into the problem of efficiency of the entire school system, involving the child, its instruction, and physical environment.

The Committee desiring to utilize the equipment and services of some of the staff of the College of the City invited me to undertake the study of the air of the New York City Schools. The invitation was accepted after I had succeeded in securing the co-operation of my colleague, Professor C.-E. A. Winslow, who subsequently was selected as chairman of the New York State Commission on Ventilation.

Our work constituted a part of the investigation assigned to Mr. Chas. G. Armstrong, the engineer to the School Inquiry Committee.

A preliminary investigation was made during the spring of 1912 after the ventilating plants in those schools having them had been shut down. For this work \$750 was allowed. The work was continued, on our recommendation, in the fall of 1912 and winter of 1913, when the various ventilating systems were in operation, with a further expenditure of about \$7,500. Neither Professor Winslow nor I accepted compensation for our services in connection with the investigation. The money was spent for the services of assistants and special apparatus. Space admits only a very brief summary of our work, the full report of which is now in press by order of the School Inquiry Committee referred to.

Our problem was to determine the quality of New York air and if possible express an opinion upon the efficiency of the several systems of ventilation in operation in the schools, which might serve as a guide in making recommendations looking toward the re-construction of some of the school buildings, or, better operation of the systems already installed, and to advise as to future construction. We were able to meet these demands in part only, some reasons for which will be clear in what Professor Winslow will say in the last paper to be presented this evening. Other reasons are presented herewith.

The systems studied were (1), window system (designated the "open window" method by the lay press); (2), the natural system, where ducts were provided, but no mechanical means for insuring a flow of air in a desired direction or regulating the speed of the flow; (3), mechanical ventilation by means of fans with heating coils in the main duct; and (4), the last mentioned provided further with a washer, which also acted as a humidifier. In some, in fact practically all, schools investigated, where mechanical ventilation was the method used, the air was taken

in at or near the street level and not filtered, except in so far as in special cases, we may regard passing through a spray of water as filtration, which it undoubtedly is. In this connection, however, it is important to note that after it became known that we had begun the preliminary investigation—or perhaps it was coincident with our beginning—the Board of Education appointed a committee headed by Hon. John Martin, to study the matter of ventilation in the schools, which committee made a very common sense report, whereupon the Superintendent of Schools, Dr. Maxwell, not only authorized, but ordered, the teachers in the schools to open the windows in whatever school they might be, at any time they deemed it desirable, it mattered not what system was in operation or how efficient it might be operating, thus placing another duty upon the teacher already overloaded with responsibility. Our field squads encountered these and many other conditions in their work. Acting under orders they made their observations of existing conditions as they found them. Of necessity, the comparative value of our investigation from a refined point of view was materially lessened. However, what we did learn proved of no little value as will become apparent to one who studies the report.

Two fundamental facts presented themselves to us at the outset; first, the quality of the air of the city itself, and second, the quality of the air in different localities of the city.

When it is considered that the children are in school 5/24 of a day for 5 days in a week for 8 months, that is to say, about 1000 hours of the total 8760 hours of the year, approximately 3/24 of their existence, while the remaining 21/24 of their time is spent in the streets, where the air is superior in certain ways and far inferior in others, and in their homes, where different features are better, but others worse, it becomes a matter of no small moment to recommend the expenditure of many millions of dollars for the installation of elaborate systems of ventilation involving the cost of maintaining them in operation when the heating plants are not going, as desirable as they may be, for the actual benefit derived.

The examination of all the 600 schools in New York was obviously out of the question, so under the advice of Mr. Armstrong, we selected 32 typical examples, ranging from modern and well managed fan-ventilated schools to older buildings in congested tenement districts, ventilated without fans, and including buildings of various sizes from one of the largest high schools to a four-room country school in Richmond Borough.

Ten of these schools were studied intensively, being visited once a week between December 2, 1912 and February 14, 1913, while the other twenty-two were visited on one or more occasions between February 14 and March 15, 1913. The latter group included some night schools.

The work was organized under three major heads, *vis.*:

I. A study of the physical and chemical condition of the air.

II. A study of the air distribution within rooms.

III. A physiological study of "crowd poison."

I. *Physical and Chemical Condition of the Air*—Those factors known to possess more or less physiological significance only were considered. They were (a) Temperature, (b) Relative Humidity, (c) Carbon Dioxide, (d) Dust, and (e) Bacteria.

(a) *Temperature*—Over 1800 determinations were made, besides some 340 daily thermograph records obtained with 12 Tycoos instruments located for various lengths of time, in different schools. The general results obtained by the sling psychrometer are shown in Fig. 1. The thermograph records will be referred to under "operation."

The data are expressed in the form of distribution-curves, the abscissae representing the observed values in each case and the ordinates the percentage of all observations falling within the limits of values indicated below. It is evident that these records as a whole indicate very good conditions. The temperature curve centers closely, as it should, about +68° F. On the whole, this result must be considered highly creditable and an

indication that the children of the New York schools for the most part enjoy good atmospheric conditions, free from objectionable overheating. An examination of particular schools, however, shows that this general curve covers up markedly different conditions in individual cases.

(b) *Relative humidity* was recorded with over 1800 observations made with the standard United States Weather Bureau sling psychrometer, swung through an angle of  $180^\circ$ .

The general distribution of results in regard to relative humidity is shown in the fourth curve of Fig. 1.

#### WIDE HUMIDITY RANGE

The range of relative humidity is seen to be a wide one. Sixty per cent of all observations, however, fall between 20 per cent and 40 per cent of saturation and the general average for all schools is 35 per cent, indicating a distinctly dry atmosphere.

We found a close correlation between outdoor temperature and indoor temperature and indoor relative humidity, closer if anything in the naturally-ventilated than in the artificially-ventilated schools. This is an important point, in view of the criticism often leveled at the supposedly abnormal air of the fan-ventilated schools. It does not make the least difference whether air is heated in the ducts or in the rooms, the same rise in temperature produces the same drying effect.

The only way to avoid dry air in the schoolroom with certainty is by means of fan ventilation, combined with artificial humidification.

(c) *Carbon dioxide* was determined (nearly 800 determinations) with an improved Petterson-Palmquist portable apparatus. It is recognized that a knowledge of the  $\text{CO}_2$  content of the air is of comparatively little value beyond measuring the rate of exchange, but we secured valuable data especially in connection with the night schools.

Our results in regard to carbon dioxide are summarized in the lowest graph of Fig. 1.

The general average value for all schools was 9.1 parts per 10,000. Sixty-six per cent of the observations fell below 8.5 parts, which may be considered a very satisfactory result on any standard. Twenty-nine per cent of the tests showed between 8.5 and 12.5 parts, which would have been considered high on the older standards established when carbon dioxide was held to be a measure of some mysterious poisonous matter in the air.

There remain 6 per cent of the tests, however, showing over 12.5 parts which are clearly excessive. These were associated with overcrowding and deficient air supply in individual rooms.

Supplementary observations made in four schools during evening sessions (when there is no artificial ventilation) showed some very high carbon dioxide values ranging, in one case with gas burning, up to 26.0 parts.

This is a special problem which deserves more attention than it receives in many cities.

(d) *Dust Particles*—Nearly 700 samples were collected by filtration through sugar with an apparatus for measuring volume by time, especially devised for us by Wallace & Tiernan (described on p. 238). After the sugar was dissolved, the dust particles were examined in an aliquot part under the microscope ( $\frac{2}{3}$  in. objective), general character noted, and counted (the standard method).

The general distribution of dust counts is shown in the second graph of Fig. 1. The largest number of samples showed between 200,000 and 400,000 particles per cubic foot. The general average for all schools was 601,000 particles and 20 per cent of the samples showed 800,000 or more, with a few values ranging up to 2,000,000 and over.

The sanitary significance of these results is probably not great. Dust particles constitute a serious menace to health in industrial establishments, grinding shops, granite cutting sheds and the like, since the hard metallic or mineral particles which are found under such conditions injure the lung tissue and often form a

controlling cause in the development of industrial tuberculosis. There is no evidence, however, to show that such particles as occur in ordinary schoolroom air have any such significance. The particles which we found were for the most part minute and chiefly organic in nature. In the counting cell they separated into two layers, the greater number, floating on the surface, being barely visible under the microscope and consisting in large part of mold spores; while less numerous particles settling on the bottom included larger shreds of vegetable fiber and inorganic matter.

(e) *Bacteria*—About 700 samples were collected by filtration through sterile sand. The sand was washed with sterile water and the bacteria plated on litmus lactose-agar, the general method recommended by the Committee of the Laboratory Section of the American Public Health Association on Standard Methods for the Examination of Air. The term "bacteria" included yeast and molds as well; all microbes, in fact, which will form visible colonies on litmus-lactose agar in five days at room temperature. The most frequent result was 25 microbes or less per cubic foot, but the high results pulled the general average up to 96. However, 68 per cent of the samples showed counts of 100 or less and only 9 per cent over 200.

These counts include all sorts of organisms from all sorts of sources, which are able to withstand drying long enough to be lifted up and blown about in the air. Most of them, of course, are of no sanitary significance, and the values, averaging under 100 per cubic foot and in most samples much less, must be considered satisfactory by comparison with the results reported by Miquel (150 bacteria per cubic foot in the air of Paris), by Tenon (40-60 bacteria per cubic foot in quiet hospital air), by Hesse (60 bacteria per cubic foot in a classroom before the students arrived, raised to 430 during the hour, and 1,000 just after the class had left), and by Soper (140 bacteria per cubic foot at the remote end of the Fulton Street Subway station, New York City).

#### BACTERIA OF HUMAN ORIGIN

In order to obtain an estimate of the bacteria of human origin which might at times include pathogenic forms, we made all our plates on litmus lactose-agar, as noted above, and isolated all red colonies which appeared on the plates.

It is well established that acid-forming streptococci are among the most abundant forms in the human mouth, while they are absent from sources which have not recently been exposed to human or animal pollution. We have found the number of these organisms in preliminary experiments one and a half years ago to be quite small. We then found among 30,000 colonies isolated from 750 plates, exposed in schools with window ventilation, only ten mouth streptococci.

In the present study, in the examination of a total of 868 cu. ft. of air, we found 260 mouth streptococci, or thirty for every 100 cu. ft. of air. The average number of mouth streptococci for the individual schools ranged for the most part between ten and thirty-five per 100 cu. ft. In one crowded school in a poor district it rose to 75 per 100 cu. ft., and in a school in a good semi-suburban district, no streptococci were found in 41 cu. ft. of air. The general average of thirty mouth streptococci per 100 cu. ft. gives a ratio of about one of these forms to 300 total bacteria.

A child breathes less than 100 cu. ft. of air during an average school period and these mouth streptococci must, of course, be far more abundant than pathogenic forms. At a rate of twenty to twenty-five mouth streptococci per day the chance of ingesting pathogenic bacteria from the air is seen to be a slender one.

II. *A Study of the Air Distribution within Rooms*—This involved some 500 anemometer readings, some 2000 temperature determinations in various parts of the many schoolrooms

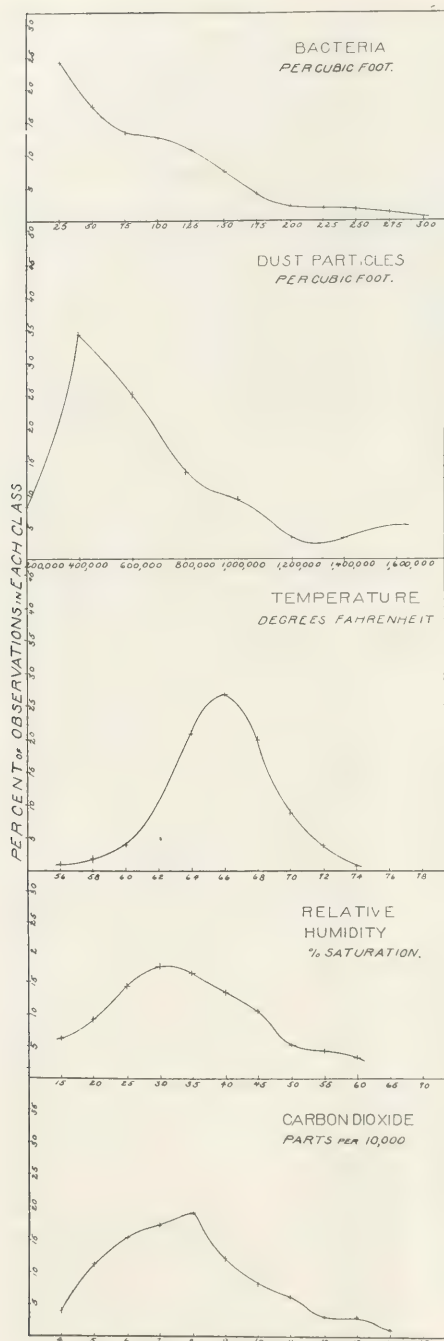


FIG. I—GENERAL DISTRIBUTION OF RESULTS FOR ALL SCHOOLS STUDIED

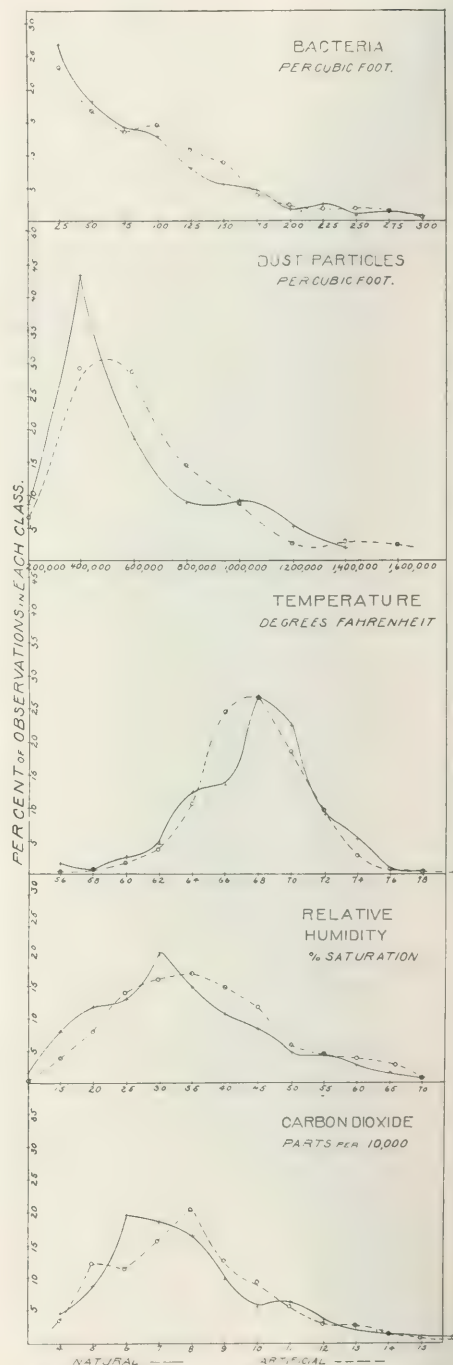


FIG. II—DISTRIBUTION OF RESULTS IN VENTILATED SCHOOLS



studied. The data obtained gave some interesting facts as to how the mechanics of ventilation work out in practice.

Inlet and outlet velocities were studied with the anemometer in 50 rooms, 25 in one of the best fan-ventilated schools (33 Bronx), 16 in four fan-ventilated schools where high carbon dioxide values had been found and 9 in four schools ventilated without fans. The amount of air supply in the fan-ventilated schools showed that in School 33 the amount was more than ample, while in the poorer school it was inadequate. For the most part we found a good plenum condition in all the fan-ventilated rooms. The very high ratios were usually in rooms with doors or windows open.

The results obtained in the naturally-ventilated rooms are not very significant, since doors and windows were freely opened. It is of interest to note, however, that in one school we found inlet velocities of 200 and 300 lin. ft. per minute without fans, maintained by unusually high temperatures of inlet air.

The circulation of air within the rooms themselves we studied by the use of smoking joss sticks and by an elaborate series of local temperature measurements. The results obtained by the use of the joss sticks in about 70 rooms were very hard to correlate. In about half of the fan-ventilated rooms there were clean-cut currents which could be traced across the upper part of the room, down the side wall opposite and back along the floor to the outlet. In an equal number of cases, however, the currents were indefinite and broken and in a few cases no currents at all could be discerned. In the rooms without fans the currents were usually very erratic, although in one or two cases a definite circulation was produced by windows open at top and bottom. In general the naturally ventilated rooms were much more subject to local drafts than were those ventilated by fans.

The local temperature observations were on the whole more valuable as throwing light on air circulation. In 24 rooms in fan-ventilated schools we found an average increase in temperature between inlet and outlet of  $4.3^{\circ}\text{F}$ .

The outlet temperature corresponds very closely to the general room average. This indicates that the outgoing air is a pretty fair sample of that in the room and that its temperature may be taken as a fair measure of that of the room as a whole.

The difference between bottom (3 ft. above floor) temperature and top (12 ft. above floor) temperatures was inconsiderable, and more variable than might have been expected. Of twenty-six rooms in which both were determined, just half showed a higher temperature at the top than at the bottom, while in the rest the upper air was cooler. The top excesses were higher than the bottom excesses, however, averaging over  $2.0^{\circ}$  instead of under  $1.0^{\circ}$ .

The slight extent of the differences observed is probably due to the fact that, on the one hand, cool air was being blown in at the top of the room while, on the other hand, the air, as it was warmed in the room, tended naturally to rise. This condition must interfere to some extent with normal air circulation and offers a certain argument in favor of upward as opposed to the usual downward ventilation.

Finally, the range between the maximum and minimum individual temperatures observed in the room is significant as a measure of general air circulation. The differences ranged for individual rooms between  $1.7^{\circ}$  and  $12.0^{\circ}$ , and averaged  $5.8^{\circ}$ , showing on the whole a fairly good mixture of the air. These observations were all made in fan-ventilated rooms.

In rooms ventilated without fans, conditions were more variable. Among eighteen rooms without fan-ventilation (that is, without a current of cool air blown in near the top) all but one showed a higher ceiling temperature, the excess in two cases being over  $11.0^{\circ}$ , and averaging  $5.8^{\circ}$ .

Another marked difference between the fan-ventilated and the artificially-ventilated rooms lies in the evenness of temperatures at different points. The range of difference between maximum

and minimum room temperatures for the fan-ventilated rooms as noted above, was from  $1.7^{\circ}$  to  $12.0^{\circ}$ , and the average  $5.8^{\circ}$ . For thirty-eight naturally-ventilated rooms, it ranged from  $1.2^{\circ}$  to  $20.2^{\circ}$ , and averaged  $7.9^{\circ}$ . Obviously, the air circulation is rather defective when such conditions exist.

It may be of interest to note that in five of the naturally-ventilated rooms, all in one building, the temperature of the incoming air was respectively,  $83^{\circ}$ ,  $86^{\circ}$ ,  $90^{\circ}$ ,  $98^{\circ}$ , and  $125^{\circ}\text{F}$ . In the latter case one of our thermometers (registering to  $130^{\circ}$ ) was burst by the heat of the inlet air the first time the temperature was taken.

#### COMPARISON OF NATURALLY- AND ARTIFICIALLY-VENTILATED SCHOOLS

For the purpose of estimating the value of fan-ventilation, as actually operated in New York schools, curves were plotted for all the schools classified on this basis and this curve is reproduced in Fig. II. Of course, it must be understood that by natural ventilation is meant simply that fans were not running. In almost all cases there were ducts and often heating coils were within them and air was undoubtedly passing through them. So, on the other hand, where fans were in operation, windows were often open and outside air passing in or out through them. The distinction is made solely on the fact that fans were or were not in operation in connection with the particular room in which each test was made.

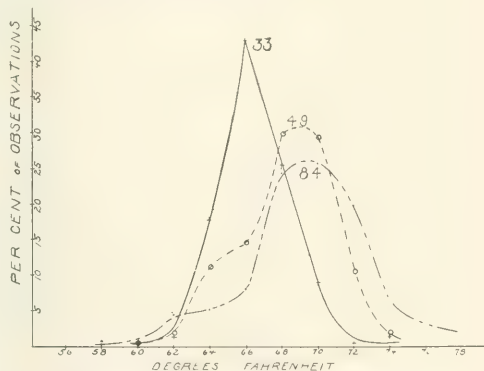


FIG. III.—TEMPERATURE CURVES, PUBLIC SCHOOLS NOS. 33, 49, 84  
33—Good Fan Ventilation 49—Naturally-Ventilated  
84—Badly Operated Fan Ventilation

The general results for the two classes of schools are on the whole remarkably alike. The fan-ventilated schools show more dust, more humidity more carbon dioxide and a somewhat more equable temperature; but none of the differences is very great or very significant.

In dust and carbon dioxide, the fan-ventilated schools appear slightly inferior to the others. In humidity they are better (if dry air be a disadvantage). In temperature they are also somewhat better, showing less observations over  $72^{\circ}$ .

So far as temperature is concerned, however, it should be noted that the curve for the fan-ventilated class conceals wide variations between the individual schools included in it. Of our ten schools more thoroughly studied, it is noteworthy that the four really good records (from the standpoint of temperature) were in fan-ventilated schools. The three wholly or partly naturally-ventilated schools are mediocre or poor; and two fan-ventilated schools are worst of all.

In Fig. III are shown typical curves for these three classes. Either almost perfect conditions or very poor conditions may be obtained with fan-ventilation according to the care and intelligence of the janitor in charge.

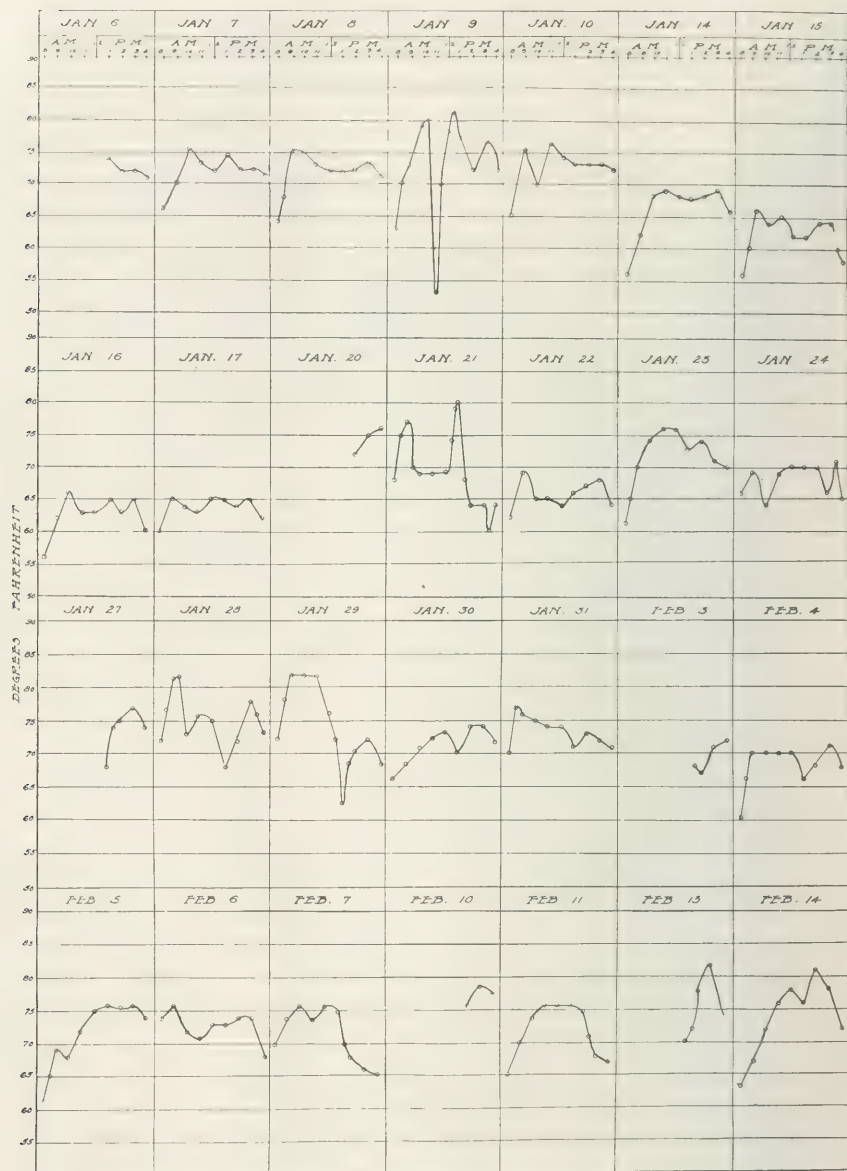


FIG. 1V—AUTOMATIC TEMPERATURE RECORDS IN A DAILY-OPERATED FAN-VENTILATED SCHOOL—PUBLIC SCHOOL NO. 1, QUEENS

On the whole it can be said that, comparing the actual condition of rooms ventilated with and without fans, New York was not deriving any material advantage from its fan-ventilation last winter as actually operated.

#### THE OPERATION OF A VENTILATION SYSTEM

A system of ventilation inherently not the best may give good results by good operation, and an excellent system may give poor results by poor or unintelligent operation. This fallible

statement was vividly illustrated in our investigation. We found certain schools of either type which had an ample air supply and uniformly low carbon dioxide values. We found other schools, of both types, in which the supply of air was inadequate and carbon dioxide figures consequently high. In the case of fan-ventilated schools this usually meant low inlet velocities (sometimes inadequate inlet areas) or overcrowding, while in the naturally-ventilated schools it meant either overcrowding or neglect to open windows.

The most striking results of careless operation were shown, however, in the matter of overheating. In the case of the naturally-ventilated schools the coöperation of both janitors and teachers is required in order to secure good results, and, where so many persons are concerned, it is practically impossible to reach a maximum of efficiency. Such results as that indicated in Fig. III for School 33 could scarcely be attained where window ventilation plays any large part.

In fan-ventilated schools, on the other hand, the whole responsibility rests (or should rest) with the janitor, and either very good or very bad results may be attained, according to his intelligence and responsibility. The continuous records obtained by our recording thermographs brought out the importance of the operating factor with startling clearness, and four of our curves are reproduced herewith to illustrate the variation which occurred (Figs. IV and V).

In order to remedy this condition we urged that a thermograph of some improved type be installed in each school building

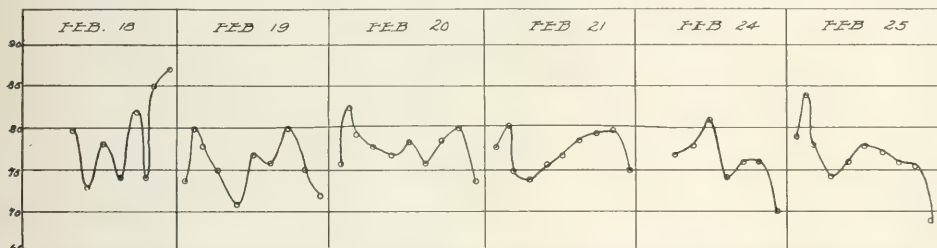


FIG. V—AUTOMATIC TEMPERATURE RECORDS IN A BADLY-OPERATED NATURALLY-VENTILATED SCHOOL—PUBLIC SCHOOL NO. 25, MANHATTAN

and that the records obtained be carefully inspected and made the basis for an efficient control of ventilating systems and janitorial service and we recommended that these records be supplemented by periodical studies of temperature and volume of air at the room inlets.

#### CRITERIA FOR SCHOOL-ROOM AIR

The chief value of these investigations lies perhaps in their possible use as a basis for comparative studies in the schools of other cities, which are greatly needed, if scientific records are to take the place of opinion in the field of school ventilation.

The results obtained in regard to dust and bacteria seem to indicate that, so far as these suspended matters are concerned, the air of the New York schools is in a satisfactory condition, without any special measures of protection, provided we regard the air of New York as good. Personally, I know the air in New York City is better than in some cities, it is also worse than in some other cities. The topographic conditions are an important factor. The general air conditions can and should be improved, for example by more extended washing down of the streets. I have not ceased in my hopes furthermore to see the city wash down its streets at suitable intervals with proper disinfecting solutions.

So far as carbon dioxide is concerned, our results indicate that it is comparatively easy, either with or without the use of fans, to keep the air in a schoolroom so changed that its carbon dioxide will average well under 10 parts per 10,000 and will rarely exceed 12 parts. This test furnishes an excellent measure of air change and under ordinary conditions such an air change is essential in order to remove odors and preserve a freshness agreeable to the senses. Where air is recirculated, however, with washing or chemical treatment to remove odors, the carbon dioxide standard may have to be relaxed still further, although it will always be of value as an index of what is going on in the way of air dilution.

III. A Physiological Study of "Crowd Poison"—In view of the claim of Rosenau and Amoss that specific proteid com-

pounds of human origin can be detected in respired air by the delicate physiological reaction of anaphylaxis, we devoted considerable attention to this point. Dr. D. R. Lucas, who conducted this part of the investigation, was able to demonstrate easily the presence of such specific proteid substances in the saliva under carefully controlled conditions, but was unable to detect them in material condensed from the breath or in air heavily contaminated by the respiration and exhalation of dogs and human beings. We were forced to conclude that "there is at present considerable uncertainty as to the presence of such specific proteid substances in demonstrable amounts in respired air and that there is absolutely no evidence of the presence of any organic substances of a deleterious nature in such air."

Similar experiments carried out simultaneously and independently by Dr. Charles Weisman at Columbia University and published as a Doctor's Dissertation have led to the even more definite conclusion that "the results of these experiments disprove the statements of Rosenau and Amoss that the breath

contains 'volatile' protein and that such 'volatile' protein is an important respiratory factor."

While subsequent investigations may prove it different, at present we may agree, in large part at least, with the conclusion reached by Flügel eight years ago, *viz.*, "Whenever in closed, crowded rooms certain impairment of health ensues, such as headache, dizziness, nausea, etc., these symptoms are to be attributed solely to heat retention."

Overheating seems to be the chief evil to be guarded against in school ventilation at present. Associated with this is regulated humidification.

COLLEGE OF THE CITY OF NEW YORK

#### THE NEW YORK STATE COMMISSION ON VENTILATION AND ITS PROBLEMS

By C.-E. A. WINSLOW<sup>1</sup>

Rudolph Hering has well said, in his recent address as President of the American Public Health Association, that the subject "of supplying suitable air to enclosed spaces, of heating, ventilating and removing foul air, is one which as yet is not sufficiently well understood in detail, and on which there are still opposing opinions. In fact, of all of the branches of sanitary engineering at the present time it needs most investigation and most study." In the last few years, however, a new and encouraging interest has been manifested in the study of ventilation problems. Among the various signs of this awakening none is perhaps more significant than the creation of the New York State Commission on Ventilation to undertake a broad and fundamental study of the physiological and mechanical problems which underlie the art of air conditioning. For the first time, in this country, at least, a sum of money is to be applied toward the solution of these problems which, though small in comparison with the magnitude of the task, is large enough to give

<sup>1</sup> Chairman, New York State Commission on Ventilation.



hope of substantial results. The Hodgkins Fund of the Smithsonian Institution has made possible the publication of a number of individual researches on the relation of the atmosphere to health which have become classics. College and health departments and committees from many societies have made important contributions to the subject. There has not before, however, been any body which could attack the whole problem under such favorable circumstances as can the New York State Commission on Ventilation.

This Commission was made possible by the assignment to its use of the sum of \$50,000 out of a munificent gift made for various social investigations by Mrs. Elizabeth Milbank Anderson to the New York Association for Improving the Condition of the Poor (Mr. J. A. Kingsbury, *Director*). The Commission was made an official State Commission by appointment of the Governor on June 25, 1913. Its members, who serve without pay, are Mr. D. D. Kimball (Ventilating Engineer), Prof. F. S. Lee (Professor of Physiology in Columbia University), Dr. J. A. Miller (of the Bellevue Medical School and Hospital), Prof. E. B. Phelps (late of the Massachusetts Institute of Technology and now Chemist of the U. S. Hygienic Laboratory in Washington), Prof. E. L. Thorndike (Professor of Psychology in Columbia University), and the writer. Its objects are "to examine and investigate the subject of ventilating systems in the public schools and other public buildings of the state, and the proper installation of the same to the end that a thorough and effective system, which will assure an adequate supply of fresh air, under the best conditions, will be maintained." In his statement in regard to the appointment of the Commission the Governor pointed out that "the problem is far from simple." He continued, "It is much more than an engineering problem, for the best scientific experts have not determined what conditions should be met by the engineers. Even the most fundamental facts which must lie at the basis of any efforts to ventilate our school buildings, have not been scientifically determined by any experiments which have been made thus far. It is not known, for example, and cannot be known without more adequate experiments than have been possible up to this time, what temperature should be maintained in public school buildings. Indeed, it has not even been proven whether a constant temperature or a varying temperature is more beneficial. We do not know scientifically what degree of humidity should be maintained in our schoolrooms.

"I am informed, also, that it has not been proven what amount of carbon dioxide in the air is possible before the air becomes detrimental to health. In other words, there is no scientific proof for some of the most fundamental factors involved in the problem of ventilation. On the other hand, I have been assured that if careful scientific studies were made with the express purpose of measuring some of the unknown factors, such studies could be reasonably expected to put us in possession of data which would enable the scientist to tell us with some degree of accuracy what those fundamental conditions are which should be maintained in schoolrooms if they are to be beneficial to the health of children."

Other speakers have so ably presented the positive results of previous studies of ventilation problems during the last ten years that I need not dwell upon what has already been achieved. We may take it as established that changes in the oxygen or carbon dioxide content of the vitiated air of rooms never remotely approach the limits at which harmful physiological effects can be produced. We may safely assume that specific organic poisons are absent from breathed air since all recent experiments along this line have yielded negative results. We may conclude with reasonable certainty that the symptoms of discomfort in a badly ventilated place are due to the physical condition of the air in respect to temperature, humidity and movement, and not to any chemical properties whatever. All

this represents solid and important progress. I wish to-night, however, rather to call your attention to the lacunae in our knowledge, which this new Commission is to try in some small measure to fill in.

In the first place, since as scientific men we must ask not only what happens under a given set of circumstances but how and perhaps why it happens, we need to know much more than we now do as to the mechanism of the bad effects produced by atmospheric heat and moisture. Through what means is the difficulty in giving off bodily heat translated into the sense of discomfort, the headache, the drowsiness and the other symptoms experienced in a warm room? There are many suggestive possibilities. One of the most striking recent hints is the observation of the English physiologist Barcroft that under the influence of external heat the dissociation curve of the hemoglobin is so altered, presumably as a result of decreased alkalinity, that oxygen is less rapidly absorbed. If this result is confirmed it may be that in a badly ventilated room we really suffer from oxygen starvation after all, not however as a result of oxygen deficiency in the air, but as a result of the effect of temperature upon the chemical properties of the blood. Allied to this problem of the causes of discomfort in stagnant, overheated air is that of the relation of such air to various diseases. Discomfort and disease may of course be due to the same factors but such is by no means necessarily the case. We know that tuberculous and anemic children improve when exposed to the influence of moving currents of cold, dry air. It would be of the greatest scientific importance and perhaps of much practical value to know by what physiological reactions this is brought to pass.

The upper limit beyond which our room temperatures should never be allowed to go is clearly indicated by the experiments to which reference has been made and it seems certain that except for old people it should be fixed at least as low as 70°. As to the lower limit, however, we are far more in doubt. In this country we are apt to consider 65° quite cool enough, while in England, rooms are usually kept 5° lower. It is maintained by some advocates of open-air schools that the unheated air of winter ranging from 50° to 0° is more desirable than either. It seems probable that the problem is complicated by the existence of a "danger zone" of temperature, low enough to cause a dangerous chill, but not low enough to stimulate the defensive reactions with which the body defends itself against more severe cold. It is certainly complicated by a considerable power of gradual acclimatization, by which the defensive mechanisms adapt themselves to a higher or lower air temperature in the course of days or weeks. It would seem, however, that there must be a certain range of temperature which is most favorable to maximum efficiency with a minimum expenditure of bodily energy. On the basis of the fundamental human instinct for keeping warm in winter I doubt very much whether this range will correspond with the chance variations of the winter temperature in a northern climate; but I am quite open to further light upon the subject.

We must distinguish between favorable conditions of normal air temperature and the possible value of sudden brief variations therefrom. It is maintained with good reason that any uniform temperature maintained for long periods may be distinctly harmful by lowering the tone of the heat regulating mechanism and by robbing the body of valuable nervous stimuli. The good effects of cold baths are well recognized and "cold air baths" may be equally beneficial. Closely allied to the question of variations in temperature is that of air movement. At temperatures over 70° F. strong air currents which may carry off the excess heat in the aerial blanket surrounding the body are essential to comfort. Even at low temperatures air currents certainly exert a pleasant and wholesome stimulating effect within certain limits. What these limits may be, however, we do not clearly know, and we

do not understand the exact nature of the bad effects produced by chilling of the body surface, particularly of the local chilling caused by what is commonly termed a draft. The value of moving air under certain circumstances is unquestioned; but so is the harmfulness of "drafts." Where the threshold lies between the two, and why it lies there, is what we need to determine.

The problem of humidity is almost as complicated as that of temperature. We know a good deal of the upper limits of high temperature combined with high humidity. We know that low humidity combined with low temperature produces grave chilling effects but where the permissible upper limit of humidity lies at a given low temperature has not been carefully worked out. As to the supposed harmful effects of low humidity combined with high or moderate temperature we are almost wholly in the realm of conjecture. We are told that schoolroom air is drier than the desert of Sahara; and as Professor Baskerville has pointed out, the air in the New York schoolrooms is certainly pretty dry. Dry hot climates, like that of Egypt are, however, sought out for their health-giving properties and the claims that the dry air of our rooms in winter overstimulates the cutaneous nerves causing nervousness and restlessness and injures the respiratory membrane so as to promote nose and throat disease, while a reasonable assumption, has as yet no firm basis of experimental observation. So far as I am aware, there are no sound data by which we may determine whether, with a temperature of 70° C., the humidity should be 25 per cent or 50 per cent or 75 per cent of saturation.

One of the first things that strikes an observer on entering an unventilated room is the odor, produced by decomposing organic matter in the mouths, on the bodies, and on the clothing of the occupants. Highly offensive to one coming in from a purer outside air, these products are usually imperceptible to those who have been in the room while they have been accumulating and whose olfactory nerves have been gradually accustomed to them. It is of course possible that even when unperceived these bodies may exert some subtle, harmful influence, but there is not the slightest evidence that such is the case. In any event it seems reasonable to demand for decency's sake that the air of occupied rooms should not be malodorous. It is somewhat an open question, however, how far such conditions should be met by ventilation and how far by a rise in general standards of personal cleanliness.

In regard to the dust content of the atmosphere, the serious danger from comparatively large particles of mineral matter such as are produced in stone-cutting, needle grinding and the like, is well established both by animal experimentation and by statistical study of the incidence of tuberculosis in the dusty trades. Whether the very minute dust particles, largely of organic nature, which to the number of a million or so per cubic foot may be found in ordinary schoolroom air have any such significance at all is another question, to which we have at present no answer. The chief argument for the use of air washers is in most cases the possibility of freeing the atmosphere from such dust particles. We know that where delicate physical instruments are in question, it is essential to wash ordinary city air. The respiratory passages are, however, equipped with an excellent mechanism for self-cleansing and it is altogether possible that the ordinary dust content of the atmosphere is a negligible factor. I do not believe that we have at present any valid reason for suggesting the washing of normal city air on sanitary grounds.

With regard to the bacteria in air, evidence is reasonably clear that they have no serious sanitary significance. Local pollution takes place by the discharge of mouth spray immediately in front of an infected person; but such spray quickly falls to the ground and does not in any sense constitute general aerial pollution. The experience of modern hospitals in which

various diseases are treated in the same open ward without cross infection, provided only direct transfer by nurses and other attendants be avoided, is reasonably conclusive on this point. The heavier dust particles deposited on surfaces do contain considerable numbers of mouth cocci and some tubercle bacilli, however; and the possibility that an appreciable danger might exist from dust stirred up in clouds as by gymnastic exercises in a dirty schoolroom seems to be well worthy of further study.

These questions to which I have briefly referred are all concerned with the physiological problem of precisely what air conditions are most favorable to the human organism. The mechanical problem of how to maintain a given set of air conditions is far better understood. Many existing ventilating plants yield unsatisfactory results, it is true, but there are three good reasons for this, none of which are related to any shortcomings in the art of the ventilating engineer. In the first place, until recently he has been told by the hygienist that the prime object of ventilation was to remove noxious gases rather than to regulate air temperature and humidity, so that he has naturally laid stress on air volume rather than air conditioning. In the second place he has rarely been given appropriations to do his work as he felt it should be done and in the third place he has still more rarely been able to count on an intelligent and conscientious operation of his plants after they have been built.

The first of these difficulties is now cleared away by the recognition on the part of all competent authorities that the chief aim of ventilation is to provide a moving current of cool air. This necessarily implies a separation of the two processes of heating and ventilation which have been so disastrously intermingled in the past. Cooling, not heating, is the task which should be closely associated with ventilating and a constant supply of cool air to remove the heat produced by human metabolism and by the combustion of illuminants is the fundamental end to be attained. It is interesting to note that Rietschel in the last edition of his standard work on ventilation bases his calculations of air volume primarily on heat removal, and on carbon dioxide dilution only secondarily and in certain specified cases. The substitution of this clear and definite aim for the old idea of mere air dilution will go far to make ventilating practice purposeful and efficient.

There are, however, still many purely mechanical problems which require further elucidation. Taking first natural ventilation or air interchange through walls, cracks, chimneys, windows and the like there is need for further data than we now possess as to the amount of leakage through walls under varying conditions of temperature and external wind movement. There is need of more exact knowledge as to the amount of ventilation through chimneys and ducts and windows with similar variables in weather conditions and as to the resulting circulation of air within the rooms.

The question of the adequacy of such natural ventilation by the admission of untempered air and the necessity or desirability of artificial or fan-ventilation is one of the most vigorously debated points in contemporaneous discussions. It is clear that with one or two persons in a large room window ventilation is adequate and sufficient. As soon as the factor of crowding comes in, however, difficulties begin to appear. In hospital wards the consensus of opinion seems to be in favor of natural ventilation. The patients have a comparatively ample air space. They are warmly covered and are doing no manual work. The windows are, or may be, under the constant control of skilled attendants. In a schoolroom these favorable factors are all wanting and in very cold weather it is usually found to be quite impossible by window ventilation to maintain properly cool conditions at the interior side without chilling those nearest the windows. In the ordinary factory workroom conditions for natural ventilation are even more unfavorable. It seems to me probable that in most schools and factories artificial ventila-



tion with tempered air (either warmed at its point of admission to the room or warmed at a central point and blown in by fans) is generally essential to good atmospheric conditions. The limits of occupancy and of outside weather conditions within which such artificial ventilation is needed deserve careful study, however. If it is possible in a room of a given type, perhaps by the use of special window ventilators to insure good diffusion and to maintain good air conditions without fan ventilation during the greater part of the year it might be reasonably maintained that the expense of artificial ventilation was hardly justified, for the removal of atmospheric odors on a few extreme winter days when the worst evils of bad ventilation could be eliminated by avoiding overheating and on the windless days of moderate temperature when window ventilation is inadequate to remove the heat produced within the rooms. I am inclined to believe that the number of days of the latter class in schoolrooms open to winds on only one or two sides is likely to be large, and that the difficulty in securing proper supervision of window ventilation is sure to limit its practical value very seriously. The whole matter, however, is worthy of open-minded investigation.

Intimately connected with this question of the limits within which artificial ventilation is necessary—and fundamental in artificial ventilation itself—is the problem of the necessary volume of air to be supplied under various conditions. On the older conception of carbon dioxide dilution it was easy to derive constants of air supply. To-day we must calculate our necessary volumes of air on the basis of heat removal. Assuming no heat loss through walls and ceilings and assuming that incoming air must not be below 60° nor outgoing air above 70°, 2000 cubic feet of air per hour will be required to take up the heat produced by a single person and 1500 cubic feet will be required to take up the heat of a single gas burner. The first figure happens to be almost exactly that deduced on the theory of carbon dioxide dilution. The amount of heat loss through walls and ceiling will modify this constant to an almost infinite degree with variations in building construction and weather conditions. Professor Bass in his experiments at Minneapolis has found it possible to reduce the air supply to a fraction of this amount without objectionable results.

Perhaps the most important mechanical problems of ventilation are those which relate to the distribution of air between different rooms and the circulation of air within the rooms themselves. German and English experiments on duct construction should be verified and extended. The mistaken claim that a ventilation system cannot be designed which will not be unbalanced by opening windows in some rooms and not in others must be set at rest. In regard to the circulation of air within the rooms there are even more difficulties. Too often a room has been treated as a box to which as a unit it was only necessary to supply a given amount of air. What happened to the air thus supplied, and how far it maintained good conditions in various parts of the room, was left to chance or to the working out of a few crudely generalized principles. I am quite convinced that in most existing installations the number of inlets and outlets is too small to ensure at all times a reasonably good distribution of air. Prof. Bass's results, to which reference has been made, were accomplished by supplying air through individual inlets at each desk. This is an extreme case but we need to know with some exactness the proper mean between this condition and the usual single inlet and outlet. In connection with this question is the mooted problem of upward vs. downward ventilation. My own personal feeling is that it will frequently be best to take advantage of the natural upward tendency of air which is being warmed by supplying cool fresh air below and removing the warmed air above as is done in some of the most successful ventilating systems now in use in auditoria and factories. The objection felt to drafts of cool air is the limiting factor in this system, however, and we must not rest on

abstract generalizations but on careful studies of the variables involved in practical operation.

The most important contributions to the art of ventilation in recent years have certainly been the experiments on recirculation of air at Minneapolis and at Springfield, Mass. If it is possible, as the theory of the newer ventilation would suggest, and as these studies seem to indicate, to use the same air over and over again, merely adjusting its temperature and humidity and washing or ozonizing to eliminate odors, the cost of operating a ventilating system may be cut from one-third to one-half and the whole practice of ventilation will be revolutionized.

Finally, there are many minor mechanical problems which require further study. The efficiency of various types of air washers should be carefully compared as has recently been done in certain installations by Professor Whipple of Harvard University. The use of ozone machines as an alternative to air washers for deodorizing deserves further consideration, although physiological investigations, both in this country and in Germany, throw serious doubt upon the advisability of this procedure. The distillation of objectionable gases from dust on heating surfaces is an interesting and important question; and there are many more to which I cannot even allude in this hasty review.

More than enough has been said, to indicate the need for light upon many of the physiological and mechanical problems which underlie the art of ventilation, and to illustrate the fact that the New York State Commission on Ventilation has quite enough to occupy its energies. We are only at the threshold of our work and have at this time only questions to ask and no answers to give. Our staff is now practically organized, however, with Mr. G. T. Palmer as Chief of the Investigating Staff and Mr. Joseph Herzstein as Secretary and we shall begin actual work before the end of the month. Through the courtesy of the Board of Trustees of the College of the City of New York two experimental rooms have been equipped in the Biological Laboratories of the College in which any desired conditions may be maintained. Here it is hoped that the fundamental physiological problems may be so worked out as to determine with reasonable definiteness what atmospheric conditions in regard to temperature, humidity, air movement and the like are most favorable to human health and efficiency. Special studies will also be made here in regard to the distribution of dust particles and bacteria in the air and the physiological effects of dusty air in promoting tuberculosis.

Through the courtesy of the Board of Education of the City of New York experimental schoolrooms are included in the plans for one of the new buildings to be completed in 1914 in which air of any desired condition can be admitted and withdrawn from any point. In these rooms the favorable air conditions determined in the City College experiments may be tested out on a practical scale and detailed studies may be made in regard to air circulation. The latter should be supplemented by special experiments on the mechanical problems of air flow and air circulation, and by tests of various mechanical devices used in ventilation, such as air washers and the like.

Coöperative investigations have been arranged for, under grants from the Commission, which will bring to it the advantage of much previous experience obtained by the leading students of ventilation problems in this country. These will include studies of certain fundamental physical problems of heat and moisture loss at the Massachusetts Institute of Technology (under Professor Phelps), observations on the results of the use of recirculated air in the International Y. M. C. A. College Gymnasium at Springfield, Mass. (under Dr. J. H. McCurdy), investigations of the physiological and psychological results of recirculated air supplied from individual inlets in a schoolroom in Minneapolis (by Prof. Bass), and records of efficiency of



factory operatives under various atmospheric conditions (by Dr. Hollis Godfrey).

The task before us is a large and important one which we approach with a keen sense of responsibility. There are three factors and only three which universally affect the life processes of living beings from one end of the biological scale to the other. These are the physical and chemical conditions of the enveloping

medium, food supply and predacious or parasitic enemies. The first of these factors, in the case of land animals, is solely a question of air conditioning or ventilation. I cannot doubt that when the ideal air conditions and the practical methods of securing them have been worked out with reasonable completeness it will mean an incalculable gain in human health and efficiency.

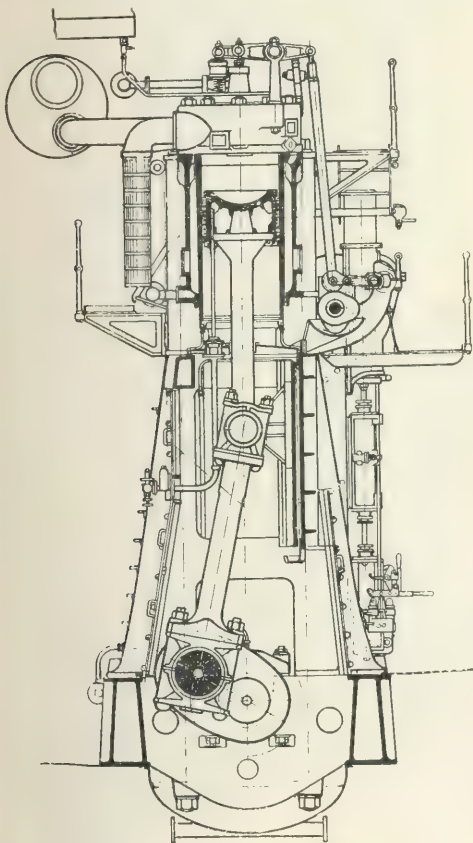
COLLEGE OF THE CITY OF NEW YORK

## CURRENT INDUSTRIAL NEWS

By M. L. HAMLIN

### THE MOTOR SHIP "FIONIA"

*The Engineer*, 117 (1914), 40, has recently published an account of the large passenger and freight vessel "Fionia" and her power plant. The "Fionia" was built by Burmeister and Wain, of Copenhagen, for the East Asiatic Co., to be used on the Bangkok route and is the ninth vessel of her kind that they have launched. She is 395 feet over all and driven by two six-cylinder 2000 h. p.



VERTICAL SECTION OF MAIN ENGINE

Diesel internal combustion engines. The diameter of the cylinders is 740 mm., stroke 1100 mm., and the speed is 100 r. p. m. Each cylinder is mounted on two columns and the columns are coupled together at the upper part on the sides by cast iron plates to give fore and aft steadiness; the guides are made fast to the

columns in the ordinary way. The bed plate is like that of an ordinary steam engine with open pits, but a steel tray is fitted underneath its whole length, and this with the light steel plate removable doors fitted between the lower parts of the columns allows forced lubrication to be used. A diaphragm piece is fitted across the top of the columns through which the piston rods pass in a light gland, and this prevents any oil which may come down from the pistons becoming mixed with the lighter oil in the crank pit.

The cylinder jackets are cast together in blocks of three and bolted to the columns in the ordinary way.

The cross-heads, connecting rods and pistons follow ordinary steam practice, the piston rod being deeply spigoted into the piston, to which it is bolted by a number of light bolts. In the "Fionia" it was necessary to give up the very nice piston cooling arrangement previously used on the "Lelandia," in which the oil was forced through the shaft up the connecting- and piston-rods and into the piston, whence it was passed down on to the guides where it was cooled to a certain extent. In the case of the new "Fionia," however, it was thought that the volume of oil necessary to cool a 740 mm. piston would present difficulties in recooling, so recourse was had to sea water which is admitted to the pistons by ordinary telescopic tubes.

Reavell air compressors are fitted on the main shaft for supplying injection air, and are supplemented by 200 h. p. Diesel compressors. Two more 200 h. p. four-stroke Diesel engines running at 225 r. p. m. are fitted for auxiliary purposes; one provides current for the auxiliary machinery, steering gear, lighting, etc., while the other acts as a stand-by. In addition to these, there is a crude oil motor simply for the purpose of lighting the ship when in port, where none of the other auxiliaries are required.

### BOILER EXPLOSIONS IN CHEMICAL INDUSTRIES IN GERMANY IN 1912

Eleven boiler explosions, exclusive of military, naval and locomotive boilers, occurred in Germany in 1912; of these, seven occurred in chemical or related industries. The *Chemiker-Zeitung*, 37 (1913), 1456, analyzes each of these cases, giving the attendant circumstances, character of the feed water, type of boiler, probable cause of the accident, etc., and these facts may be summed up as follows: All seven boilers were horizontal; in two cases the accidents were due to the water being allowed to run low through carelessness; in the other cases the accidents were caused by weakness resulting in the opening of seams, aided in one case by local overheating due to incomplete removal of boiler scale. In the seven explosions eight persons were killed, one accident only not proving fatal.

### BENZOL IN GERMANY

In connection with the liquid fuel campaign it is interesting to learn from the *Jour. of Gas Lighting and Water Supply*, 124, (1913) 1004, that there are now upwards of seventy German makers of benzol represented in the German Benzol Association. An important thing from the motorists' point of view is that

these firms all produce benzol of uniform quality. Distribution of the benzol is performed by some 1100 sale depots scattered through Germany. The price at which the benzol is sold is fixed, and averages 40 per cent lower than the price of petrol. This being true, the latter can not surely maintain its present price much longer, in view of the favorable experiences with benzol for motor use. It is stated that the associated firms referred to have this year produced 140,000,000 kg. of benzol, the entire quantity being obtained from German coal. The coke ovens are responsible for the greater part, and there are signs of further quantitative progress in the production of coke, which will in time supplement the supply of benzol.

## DOUBLE SCISSORS CROSSING IN ROLLED MANGANESE STEEL

There has recently been constructed at the works of Edgar Allen & Co., Ltd., Sheffield, England [*The Engineer*, 117 (1914), 78] for the Buenos Ayres Great Southern Railway, a layout with remarkable features. It is a double scissors cross-over built up entirely of rolled manganese steel rails, and is claimed to be the largest and most intricate junction ever constructed of this material. The entire layout weighs upwards of 100 tons and is about 145 yards long.

The application of rolled manganese steel to railway work is a development of the use to which this material has been put in the tramway world. Although the initial cost of manganese rolled-steel rails is much higher than that of ordinary steel, the life of the former is much greater than that of the latter, so that the expense and trouble of frequent replacements are avoided. Manganese steel is so tough that it may be bent double while cold without fracture, and yet is so hard that it effectually resists cutting by tools, while its resistance to abrasive wear is remarkably high. Rails of this material have been subjected to very severe tests on one of the London electric railways, and the results under the most trying conditions have shown that the durability is far greater than that of other kinds of rails previously used in similar situations.

The layout comprises eight sets of 18 ft. switches, four sets of 12 ft. slip switches, twenty acute crossings and closure rails, forming eight turnouts and eight diamonds, two of which have slip roads; the whole when connected with the closure rails forms a complete double scissors cross-over.

## ANCIENT NORSE IRON NAILS

A report in *Chem. Ztg.*, 37 (1913), 1599 of the Polyteknisk Forenings Kemikergruppe, Kristiana, on chemical methods adapted to preserving wood antiquities, makes the following statement about nails in a Viking ship: "While the original old iron nails with which the wooden parts of the ship are held together have remained bright and untarnished, several new ones which had to be used in assembling the vessel have already rusted. The cause of the great durability of the old iron, proof of which is also given by the fully preserved anchor, will be investigated by a special commission."

In connection with this investigation, C. Hugo reports in *Chem. Ztg.*, *Chem.-Tech. Rep.*, 37 (1914), 13 that a great iron kettle from the Norwegian iron works at Lesjeskogen, which were in operation between the years 1652 and 1812, was used by him and others in that place in 1886 and following years as a wash kettle, and although it stood in the open and was often left full of water, it remained completely free from rust as did the clothes washed in it. There are probably still in Romsdalen large quantities of the ore used in these works. [*Teknisk. Ugeblad*, 1913, No. 20, p. 200.]

## RUBBER STATISTICS

The *Chemiker Zeitung*, 38 (1914), 96 gives some interesting statistics of rubber production on the island of Java and out-

lying possessions; after a summing up of the general situation, the following figures appear, the amounts being given in metric tons:

TOTAL EXPORTS OF RUBBER FROM JAVA			
To	1910	1911	1912
Holland.....	39	181	794
England.....	8	99	433
Belgium.....	13	15	63
Remainder of Europe.....	6	6	10
United States.....	1	22	9
Singapore.....	3	25	3
Other countries.....	1	12	10
Totals.....	71	360	1322

EXPORTS OF RUBBER FROM THE OUTLYING POSSESSIONS			
To	1910	1911	1912
Holland.....	45	63	260
England.....	17	22	108
France.....		9	
Belgium.....	70	21	91
Germany.....	185	56	15
Penang.....	471	479	1176
Singapore.....	1859	1195	1074
Other countries.....	4	2	13
Totals.....	2651	1847	2737

TOTAL WORLD PRODUCTION OF RUBBER			
From	1911	1912	1913
Brazil.....	39,000	40,500	40,000
West Africa.....	15,000	13,800	13,800
East Africa.....	5,300	4,000	4,000
Central America.....	2,500	2,500	2,500
Plantation rubber.....	14,200	28,500	38,000
Guayule.....	9,200	7,000	7,000
Djelutong.....	2,800	2,700	2,700
Totals.....	88,000	99,000	108,000

## THE CHEMIST IN BRAZIL

According to *Chem. Ztg.*, 38 (1914), 57, only the simplest chemical products are manufactured in Brazil. There are many successful pharmacists but few chemists. The local technical schools are only beginning to teach chemistry and the Brazilians know almost nothing of professional chemists. The chemist is generally expected to know all trades and arts. Wages are fairly high but are consumed by high living expenses, doctor's bills, etc. The climate is unhealthy and dangerous to many: sanitary conditions are generally poor.

Chemists are urged to investigate the financial standing of firms offering positions and to insist on written contracts, as well as a guarantee or salary paid in advance. These precautions are necessary on account of the uncertain legal conditions in Brazil. Many chemists have gone to Brazil only to find their company already dissolved or bankrupt. Yet Brazilians are very generous when successful and in many instances have been known to give bonuses far in excess of regular salaries.

A knowledge of Portuguese is necessary, though the educated population speaks French. German is used a little in the South but is nowhere popular.

Sulfuric acid is manufactured at Sao Paulo, by the chamber process, from North American sulfur but competition is very severe on account of the cheapness of the imported acid.

The brewery industry is chiefly in the hands of Germans. The light products are most successful, but the price is high—18 to 20 cents per pint.

The large quantities of banana leaves, palms, etc., available would support a first-class industry in cellulose products but none exists as yet. Textiles are chiefly cotton and though the industry flourishes there are still many technical difficulties to be overcome. Glass and matches are made in many sections of the country. The brick and artificial stone industries are developed to some extent, but very little is done in the earthen-

were line though kaolin deposits are abundant. [The rubber industry was discussed in *Chem. Ztg.*, **35**, 1303 (1911).]

The iron industry is quite undeveloped. The ore is very pure, rich, and easily smelted but a suitable fuel is lacking. It is reported that an English firm has a concession to build several blast furnaces. Coal for gasworks, railroads, etc., is imported chiefly from England and charcoal is made by the peasants for their own use. There is one modern charcoal kiln near Rio de Janeiro and another near Sao Paulo.

Rich manganese ores are abundant but a market is lacking, as is the case with other possible products. The government is beginning a survey of its mineral resources. Oil and coal of very poor quality occur in quantities in the state of Sao Paulo and elsewhere. Almost all the necessary minerals for a solidly founded series of chemical industries are to be found in Brazil: only the necessary capital and spirit of enterprise are lacking. Much in these lines is looked for from North America and England, from whence financiers and large companies have begun a systematic campaign for concessions.

### INDUSTRIAL ACCIDENTS IN 1913

Information collected from all available sources by the Prudential Insurance Company shows the total number of persons killed in American industries in 1913 to be about 23,000 in a total of 38,000,000 employed. The following table was made up from available information:

OCCUPATIONS	Number employed	Fatal accidents
Agricultural pursuits.....	12,000,000	4,200
Building and construction.....	1,500,000	1,875
Coal mining.....	750,000	2,625
Draymen, teamsters, etc.....	686,000	686
Electricians (light and power)....	68,000	153
Fisheries.....	150,000	450
Lumber industry.....	531,000	797
Manufacturing (general).....	7,277,000	1,819
Metal mining.....	170,000	680
Navigation.....	150,000	450
U. S. Navy.....	62,000	115
Quarrying.....	150,000	255
Railroad employees.....	1,750,000	4,200
U. S. Army.....	73,000	109
Street railway employees.....	320,000	320
Telephone and telegraph (including linemen).....	245,000	123
Watchmen, policemen, firemen..	200,000	150
All other occupied males.....	4,678,000	3,508
Total males.....	30,760,000	22,515
All occupied females.....	7,200,000	540
Grand total.....	37,960,000	23,055

The probable number of serious injuries, causing more or less prolonged absence from work, was estimated at 300,000.

### PROCESSES FOR FIREPROOFING WOOD

Consul-General John L. Griffiths, London, England, states that considerable attention has been given in the United Kingdom to the best method for fireproofing wood, especially in connection with railroad construction. The following process, it is claimed, has received the favorable consideration of the British Admiralty: The wood is placed in large iron cylinders having hermetically sealed doors. The wood is steamed, and under vacuum the air and moisture in the pores of the wood are removed and the sap vaporized. The fireproofing solution is then run into the cylinders, and under pressure forced throughout the pores and fibers. Subsequently the water in the solution is evaporated in drying kilns, and the chemicals, in minute crystal form, are left embedded in the wood. When heat is applied, these crystals expand to many times their original size, forming a glassy coating to the fibers of the wood which excludes the oxygen in the air. In time the heat causes the crys-

tals to collapse, but further crystals in the wood immediately expand, and the same process of resistance against fire continues. The chemicals used are antiseptic and preservative, consisting chiefly of phosphate of ammonia. As a result of the treatment, the life of the wood is also lengthened, for the cause of decay (sap water) is eliminated. This process is claimed to be especially satisfactory, inasmuch as the material treated is not saturated with a solution of salt, nor are such chemicals used as tungstate of soda, sulfate of ammonia, sulfate of alumina, alum, etc., which invariably cause discoloration of the wood, corrosion of metals, destruction of fibers, and prevent satisfactory painting or polishing. After this treatment, the wood can be worked, nailed, glued, painted, polished, etc., as though it had not been subjected to any special process. All kinds of timber can be treated, including oak, teak, deal, pine, mahogany, walnut, beech, birch, ash, maple, whitewood, pitch, pine, larch, etc.

The first railway company to take advantage of this process was the Underground Electric Railways of London, and at the present time it is stated that the woodwork of all the cars of the company has been subjected to the treatment. It is also stated that after exhaustive tests the British Admiralty has adopted the process, that the company is engaged in fireproofing large quantities of wood for 70 motor boats for the British warships *Indomitable* and *Monarch*, and that the two new super-dreadnoughts now building, the *Queen Elizabeth* and *Warspite*, are to have their woodwork fireproofed by this process.

The company using the process states that as a result of the recent disaster at Aisgill, the Midland Railway (on whose system the accident occurred) has requested the fireproofing company to submit a tender for erecting a fireproofing plant at the company's works in Derby, and that, pending the erection of such a plant, the company has sent 144,000 feet of timber to be treated by the fireproofing company.

The cost of rendering wood fireproof by this process is a uniform one of 73 cents per cubic foot, for all woods excepting oak and teak, for which the charge is 85 cents per cubic foot.

There is another fireproofing process, known as the "Snowdon process," the chief feature of which is a chemical mixture, but the formula is not disclosed. By the use of this mixture it is claimed that woodwork and all manner of fabrics may be rendered non-inflammable and insect proof. In the case of wood already in position, it may be painted or washed with three or more coats according to density, when the solution penetrates to a depth of about one-eighth of an inch. When treated prior to construction, the wood is usually soaked in the solution in tanks, but if it is desired to render the wood fireproof throughout, pressure cylinders are used to force the liquid into every fiber.

### GERMAN UTILIZATION OF IRON-FURNACE SLAG

Consul-General A. M. Thackara reports, from Berlin, that the utilization of iron-furnace slag is well developed in Germany, and the problem of its further utilization is receiving the attention of the Prussian Government and the Association of German Iron Founders. In solid form it serves for highway and railway construction and as a body material for concrete; granulated, it is used for making building blocks, bricks, tiles, etc., and for the manufacture of cement. Slag is also employed to a lesser extent as a raw material in glass-making and in the production of artificial marble and artificial pumice stone.

Experiments have been made in the past with the use of slag paving blocks, but little or nothing seems to have come of them. The usual practice is to use slag in rubble form for road-making, the road being constructed after the system of macadam, the slag simply replacing the usual crushed stone. Its use ceases to be economical as soon as any considerable transportation charges are involved.



According to the Association of German Iron Founders, opinion varies as to the value of slag as ballast for railroad tracks. A number of German railroad administrations, particularly that of Alsace-Lorraine, use large quantities of slag as ballast, while others still regard its use with skepticism. One technical officer states that no opinion as to the relative durability of slag and hard-stone ballast is possible as yet, owing to the comparatively short time the former has been in use.

At the behest of the Iron Founders' Association, the Prussian Minister of Public Works has ordered exhaustive tests of slag concrete to be made at the Royal Prussian Material-Testing Station near Berlin. Investigation will be made as to reliable methods for determining the availability of particular slag for use in concrete. The test will extend to (1) observation of slag pieces left in the open air to determine changes in exterior appearance, volume, specific gravity, etc.; (2) chemical analyses; (3) tests of the compressive strength of rich and poor concrete mixtures, made of Portland cement and broken slag, the blocks to be tested having been exposed to air and water for varying intervals and under varying conditions; and (4) observation of the behavior of pieces of steel embedded in slag concrete blocks with special reference to rusting. The tests will continue for a number of years, but it is possible that a report may be published at the end of the first year.

Slag sand obtained from the granulation of basic slag has hydraulic properties and serves for the production of building blocks, bricks, etc., and of cement. One system of granulation is by cold water; another by air. Another is covered by a patent, according to which the hot, fluid slag is granulated by sprinkling with a salt solution; it does not appear, however, to have been put to any considerable practical use.

It is said of bricks made from slag that, as compared with glazed earthen bricks, they have a greater porosity and accompanying permeability. This is said to suit them especially for the construction of dwelling houses, as their strength increases with age.

#### IMPORTANT PROCESS FOR PURIFYING GAS FROM SULFUR COMPOUNDS

Charles Carpenter, chairman of the South Metropolitan Gas Co., London, describes in a paper prepared by him for the "Société Technique de l'Industrie du Gaz en France" a process of purifying gas from sulfur compounds which appears to have yielded truly remarkable results.

Mr. Carpenter, whose position is supported by Mr. Evans, the company's chief chemist, declares that it is possible to effect a reduction of the sulfur which is ordinarily left in so-called purified gas by more than 70 per cent, and this without causing any appreciable deterioration of the illuminating or calorific power of the gas, and at a cost of less than half a cent per 1,000 cu. ft. This is accomplished by passing the gas over heated nickel, deposited by the reduction of its chloride or other salt, on refractory material, the catalytic power of the metal causing the reaction to take place at a lower temperature than had hitherto been necessary. The finely divided condition of the metal also provides an extensive contact surface, so that practically the whole of the impurity in the gas is successfully acted upon. It furthermore is stated that when the process came to be applied in the works—on a small scale at first—it was found that to attain the best results with economy, it was necessary to give the gas a preliminary heating before submitting it to the contact material. By improvements and enlargement of plant, such perfection is claimed that since January last the whole of the gas produced at the company's works has been successfully treated, and a new plant now is being erected with a maximum production of 25,000,000 cu. ft. per day.

##### CARPENTER'S PROCESS

Mr. Carpenter found that the best conditions were obtained

by using balls, one inch in diameter, impregnated with reduced nickel obtained by the reduction of the chloride in a stream of hydrogen. The gas was preheated to 212° F. below the temperature of the reaction before its contact with the catalyzer. This enabled the retort to be kept at 932° F. The installation worked for four months, the carbon deposited being burned out by a current of air once a week. During that period 3,500,000 cu. ft. of gas were treated and the sulfur was reduced from 38.675 to 12.031 grains per 100 cu. ft.

An installation was then put up comprising forty reaction tubes twelve feet long and six inches in diameter, through which the gas passed in ten streams. The preheating of the gas was effected by 230 tubes, 2 inches in diameter and 24 feet long. Regenerators enabled the gas to be heated in these to any required temperature. This installation, capable of treating 2,000,000 cu. ft. of gas per twenty-four hours, had been at work since November, 1911, and the catalyzer remained active. The quantity of sulfur at the inlet had been, on the average, 31.94 grains per 100 cu. ft.; at the outlet 8.45 grains; a mean reduction of 73.5 per cent. Since its erection, 29,000,000 cu. ft. from 23,673 tons of coal had been treated. The costs (not including the secondary purification from H<sub>2</sub>S) had been for fuel 0.0728, for wages 0.0188, for interest, sinking fund and repairs, 0.0830 in cents per thousand cu. ft. of gas.

The Old Kent Road Works of the South Metropolitan Gas Co. has an installation capable of dealing with 10,800,000 cu. ft. per day. This installation has been divided into five units, fed with heat by a producer, so that the temperatures may be easily regulated. The arrangement provides for putting one unit out of action for the regeneration of the catalyzing material during the period of the greatest output. The combustion chambers are placed between the reaction retorts or tubes and the preheating tubes, and the flow of combustion products can be regulated in one or the other direction. In practice it is found necessary to regulate it only in the direction of the preheater. It may be considered that the function of the heating arrangement is to raise the temperature of the gas up to the point necessary for the reaction and to prevent, during the passage of the gas through the catalyzer, any fall of temperature due to radiation. The gas passes first through a couple of regenerators, counter-current fashion, then through the heating tubes and on to the catalyzer tubes; then it returns to the regenerators and gives up its heat to the gas newly arriving. Thanks to the progress made in the preheating, its temperature can be maintained at 770° F. before reaching the catalyzer; consequently the temperature of the latter has been reduced from 932° F. to 806° F.

The maximum content of sulfur was, before treatment, 62.86 grains per 100 cu. ft.; minimum, 16.01; average, 40.34 grains. After the treatment, maximum 8.71, minimum 5.82, average 7.79 grains. Since this installation was set in action, up to April 21, 1913, 650,000,000 cu. ft. of gas, from 50,800 tons of coal, had been treated. The quantity of CS<sub>2</sub> broken up corresponds to 13½ tons of sulfur, or 42 tons of sulfuric acid. Many tests have been made to find whether nickel-carbonyl was present in the gas; but no trace of deposit of nickel in a hot tube has been obtained. It is an established fact that nickel-carbonyl is completely decomposed at 392° F.; but care is taken never to let the gas touch the catalyzer unless the latter has a temperature above 572° F. The reaction has been conclusively determined by laboratory experiments to be



When pure materials are used, the carbon is deposited on the catalyzer in the theoretical quantity.

This carbon diminishes the activity of the catalyzer by protecting it from contact with the gas; the loss of efficiency is shown by daily chemical tests. Each unit goes on for thirty days before it appears necessary to burn off the carbon deposited.

Burning off this carbon requires careful handling and a temporary lowering of the temperature. It lasts over a period of four or five days, in such fashion as to keep the temperatures below the limits at which the metal of the tubes might be injured. The burning-off is complete when the emergent gases contain no carbonic acid. Calculating from the amount of  $\text{CO}_2$  obtained, the amount of carbon deposited would appear to be, in some cases, some 50 per cent above the calculated quantity. This excess may be due to the decomposition of hydrocarbons; but it is negligible in amount, as is shown by the following table of data:

	Before treatment	After treatment
Lighting power, English candles...	14.05	14.05
Heating power, B. t. u. per cu. ft.	590.0	594.0
Naphthalene, grains per 1,000 cu. ft.	45.5	47.2
HCN, grains per 1,000 cu. ft.	222.5	187.7
Carbonic acid, per cent.	1.82	1.80
Hydrocarbons	3.01	3.79
Oxygen	0.27	0.07
Carbonic oxide	8.85	8.62
Methane	26.62	27.45
Hydrogen	52.45	52.19
Nitrogen (by difference)	6.38	6.08

## NOTES AND CORRESPONDENCE

### SYNTHETIC RESINS

*Editor of the Journal of Industrial and Engineering Chemistry:*

IN THIS JOURNAL, 6, 167, there appears a criticism by Dr. Leo H. Baekeland of an original paper entitled "Synthetic Resins," which was published by the authors in THIS JOURNAL, 6, 3. We are sorry that it is necessary for us to answer Dr. Baekeland's criticism but because of the erroneous impressions which may have been created in the minds of those who have not studied the subject matter of phenol condensation products at great length, we take the liberty of submitting the following statement:

Dr. Baekeland writes that the Industrial Fellowships are paid for "in the interests of purely commercial enterprises." Not only is this not true of a number of the Fellowships, but it may be stated that every Fellowship applies itself to a certain extent to purely scientific problems which have no ulterior remunerative consideration, and many of the results of these purely scientific researches are already known to our readers through the publications of THIS JOURNAL. We presume that the Doctor does not believe an original paper would be of less value if it came from a purely commercial laboratory, such as his own, rather than from the laboratory of a State University.

The Doctor takes issue with the authors on the meaning of the Wetter patent as to whether it is the "wet process" or the "dry process." We can only state that the whole context of the Wetter-Lebach Patent is for the wet process and that it is impossible for hexamethylenetetramine to yield formaldehyde in the presence of anhydrous phenol and Wetter-Lebach states definitely that formaldehyde may be replaced "by substances which yield formaldehyde, such, for example, as hexamethylenetetramine;" the conclusion is very easy to draw. If the hexamethylenetetramine yielded formaldehyde, there must have been water present during the reaction.

It is unthinkable to the authors, who have worked for four years on this dry reaction that such a well-known chemist as Dr. H. Lebach did discover the anhydrous reaction between phenol and hexamethylenetetramine and that in the face of this discovery he did not take out basis and process patents on the reaction and the resulting resins. The position of the patent office, as Dr. Baekeland undoubtedly knows, is that the Wetter process is a wet process.

The Doctor intimates that "the authors show a fertile imagination" when they state "that the resins formed have very great commercial possibilities," and yet at the end of his criticism he assures us that these resins are identical with those formed by the wet process. While freely admitting that the wet process product of Dr. Baekeland and others has proven commercially valuable, the authors have no hesitation in stating that the dry process product which they have subjected to quite exhaustive tests is far superior for many reasons, some of which are mentioned herein.

With reference to raw materials, the process of producing hexamethylenetetramine from formaldehyde and ammonia

with the removal of water from a crystalline material, such as hexamethylenetetramine, is surely not as difficult as the removal of the water and condensing agent from a resinous material such as phenol condensation products made in the wet way. The ammonia is not lost in our dry process but may be collected quantitatively and used over and over again indefinitely.

Dr. Baekeland states that "Bakelite" is a registered trade mark for phenolic condensation products. If so, the Doctor doubtless is entitled to its exclusive use as a trade mark on any such condensation product, whether involving any discovery of his or not. One should not confuse the trade mark, however, with the question of such discovery or inventive contribution to the art as may have been made by the user of the trade mark; and in this connection it is to be borne in mind. If our definition of the word Bakelite is "narrow and arbitrary," the Doctor's definition of his own products is too broad to be of any value when he says "Bakelite is a registered trade mark for phenolic condensation products." Such a definition would include saligeno-saligenin and saliretin resins which were made by Beilstein and Seelheim in 1816 and by Moitessier in 1866, and were well-known substances probably before the Doctor was born. If Bakelite is to be used simply as a generic term for all condensation products, the meaning of the word is reduced to a minimum, because it would then include the worthless, permanently soluble, fusible products as well as the infusible, insoluble porous products made without the use of counter pressure. And such a term would indeed include such phenolic condensation products as the resins patented by Smith in 1899, Luft 1902, Blumer 1902-3, Fayolle 1903-4, Story 1905-8, DeLaire 1905, Baeyer 1907, Helm 1907, Knoll 1907, Lebach (Knoll and Wetter) 1907-8, Grognot 1908, all of which patents were taken out before Dr. Baekeland entered the field.

Our definition of the word Bakelite was from a purely scientific standpoint and had nothing whatsoever to do with its uses as a registered trade mark. We made a serious attempt, however, to use the word as defined by the Doctor in his earlier publications.

The experiments devised by us showed that dry hexamethylenetetramine and dry phenol heated together evolve no water and have "more than a theoretical significance." These experiments were designed especially to clear up the erroneous statements<sup>1</sup> which appear in recent literature to the effect that large quantities of water are produced during this reaction between phenol and anhydrous hexamethylenetetramine.

Dr. Baekeland objects when the authors describe a method for changing a porous mass of their material into a solid uniform body by welding together the ground-up material in a hot hydraulic press. This objection lies in the fact that we have not cited his U. S. patents, Nos. 939,966 and 942,700, wherein he described such a process accurately for molding his resin produced by the wet process. There is no claim made in the

<sup>1</sup> Baekeland, THIS JOURNAL, 4 (1912), 741.

article to this process as being new. The matter of molding powdered materials in a hot hydraulic press was known long before the discovery of our own materials or Dr. Baekeland's discoveries. The method is given simply to show that the porous material which Dr. Baekeland stated was of inferior value commercially can be made into homogeneous solid material which compares favorably with the best resins produced by the wet process, if we accept his own tables of the two materials.

We take decided issue with Dr. Baekeland when he makes the statement that the evolution of the ammonia is not a possible method for following the reaction between a phenolic body and active methylene groups and is "only true in case phenol is in large excess." The reaction may be followed easily by measuring the evolved ammonia when the phenol is not in excess at all, e. g., when 6 mol. of phenol to one mol. of hexamethylenetetramine are present. We intend to discuss this in a later paper and we propose to show that the reaction is very easy to follow if carried on in the presence of ethyl alcohol, amyl alcohol or certain other solvents.

The Doctor intimates that we have dealt unfairly with Dr. C. P. Steinmetz, of Schenectady, in not mentioning in our paper the fact that Dr. Steinmetz had also prepared synthetic resins from anhydrous phenol and dry hexamethylenetetramine. However, Dr. Baekeland is in possession of the knowledge that we had made basic patent applications for these resins long before Dr. Steinmetz conceived of them, according to his sworn statement in the patent office. As prior discoveries in the art, it was not incumbent upon us to give Dr. Steinmetz credit for what was clearly our own invention. The Patent Office has ruled that Dr. Steinmetz is not the first inventor, and the office has also ruled that the interference in which Dr. Baekeland was involved should be dissolved, although this matter is now pending an appeal. Indeed, every claim made in the interferences was taken verbatim from our earlier applications.

The Doctor calls upon us to describe at greater length the qualities of the rods which we have in our laboratories which are two feet long and one and one-half inches in diameter. We are prepared to say that the tensile strength, crushing strength, dielectric properties and chemical inertness compare favorably with any of the products we have been able to produce from either the dry or wet process where a counter pressure was used.

At this time we do not deem it expedient to give the methods by which the rods were produced.

The table of analysis published<sup>1</sup> on page 11, column 1, is given with one specific idea in mind, *viz.*, to show that the chemical individual, phenyl-endeka-saligeno-saligenin is one of the principal intermediate products of all these reactions between phenolic bodies and active methylene bodies and also with other data went to show that phenyl-endeka-saligeno-saligenin was the particular intermediate product which transformed into the final insoluble resin. There was no attempt made to give an analysis of our most insoluble resins as the time required for analysis was too long, owing to the slow disintegration of the resin by the caustic and it was the object of the authors to produce a purely scientific treatise of the subject without discussing at unnecessary length its technical values.

The apparatus described<sup>1</sup> on page 11 for determining whether water is set free when hexamethylenetetramine reacts with an excess of phenol also finds objection from Dr. Baekeland. He believes the condenser marked "8" is the best means for preventing any water from entering the train of absorbing tubes. This we may concede without detracting from the value of the experiments. We are indeed very sorry the Doctor did not read the article more carefully. If the Doctor will again read the article he will see that we are trying primarily to absorb nitrogen compounds and not water and we were able to account

for all the nitrogen in the hexamethylenetetramine present up to 99.5-100 per cent. The reaction does not come under the class of organic reactions of which Dr. Baekeland speaks which are considered quantitative when they lack 5 or even 7 per cent of the full 100 per cent.

Now, if the ammonia be evolved quantitatively there remains no reasonable chance for the remaining methylene groups and the dry phenol or the phenol less two of its hydrogens to yield water as a by-product during their reaction.

The condenser was the shortest type allowable which would guarantee a condensation of the phenol and a return of the same to the flask. Water, if it had been formed, would not have returned completely to the flask which was heated to 185° Centigrade, but it would have passed over in part at least into the train of absorbing tubes; or if it were formed in quantity and returned to the flask, it would have shown itself readily in either of two ways. Each drop as it fell from the condenser would have evaporated rapidly with a sizzling sound such as a lower boiling liquid makes when it falls upon the surface of a higher boiling liquid (which is actually boiling), or, which is more probable, it would have shown in a whitish ring around the top of the boiling liquid as the water in condensing ran down the sides of the flask and precipitated temporarily the resins out of the phenol. Such phenomena were not noticeable in any of the experiments.

Whatever may be Dr. Baekeland's objection, the fact remains indisputable that no water is formed during the reaction between anhydrous phenol and dry hexamethylenetetramine.

The experiments with anisol call forth some rather strange speculations on the Doctor's part. The non-reactivity of anisol and hexamethylenetetramine with each other when heated together and their activity when in the presence of phenol excites the Doctor. We feel like apologizing for having to point out that this is one of the commonest classes of reactions known where a substance A and a substance B do not react readily with each other but react readily in the presence of a third substance C. Indeed the very example the Doctor cites is among the most interesting in this respect. If we take pure meta-cresol and pure hexamethylenetetramine and let them react together they produce a resin which gives an inferior lacquer. The lacquer thus produced, heated for thirty minutes at 180° Centigrade, will darken and disintegrate in aqueous normal caustic solution in 150 minutes and darkens and dissolves in acetone in two hours while, if we accept Dr. Baekeland's statements, the meat-cresol in the presence of sufficient amounts of other cresols, will produce a resin which gives a lacquer film which is not attacked by caustic in 90 hours. We cannot understand why the Doctor accepts his own meta-cresol experiments and throws away our experiments with anisol. But we shall enter into a discussion of the relative merits of these lacquers in a later paper which we now have ready for publication.

The Doctor complains that his molecules do not obey him in the wet reaction so well as do ours in the dry reaction. We agree with the Doctor entirely on this point. We also found the wet reaction very hard to follow chemically while the dry reaction has considerable of the "Prussian Soldier" about it, especially in the precision with which it may be made to conform to orders. There are no deserters among the methylene groups in the hexamethylenetetramine—none of them are volatile—and none of them need to be pressed into service.

The tables with which the Doctor has concluded his criticism are misleading as he has arbitrarily selected examples from our tables and arranged them without regard to the original context. The tensile strengths for our anhydrous resins have no meaning, as no data is quoted of the conditions under which they are taken. The numbers quoted are neither the highest nor the lowest, nor the average of those we have published. But if the Doctor will read the paper again, carefully, he will

<sup>1</sup> THIS JOURNAL, 6 (1914), 11



see that the numbers given in each table were given for special reason, *viz.*, to show the effect of time of heating, temperature, per cent rubber product present, etc., upon the final resins.

Indeed, we have tensile strength tests on our transparent almost water white materials which run higher than any of our published results (*i. e.*, from 5,000 to 6,200 lbs. per sq. in.), but since they have no bearing upon the scientific data given in our preliminary paper, we have not submitted them until now for publication.

There are many possible differences between our synthetic resins and the synthetic resins produced by the wet process which have not been mentioned in the Doctor's criticism; and it is to be carefully borne in mind that these very differences are the determining factors in many of the lines of industry in which our product is finding a market.

- (1) The rate of discoloration in daylight or direct sunlight.
- (2) The rate of disintegration in caustic or alkaline solutions.
- (3) The solubility or discoloration in alcohol and acetone solutions.
- (4) The effect of the lower fatty acids upon the resins, such as formic.

(5) The ability of the resins to withstand shock as in rapid valve work, under high pressure.

(6) The presence of free phenol in materials used for pharmaceutical apparatus.

(7) The presence of water as a by-product in the final transformation of the resins, especially in large impregnated armatures.

These are only a few of the possible and real differences between our anhydrous resins and the wet process resins.

We cannot close this reply without pointing out another of the Doctor's errors. He concludes that our resins are identical with his resins, but this conclusion is offset by his statement that he obtained by the wet process (1) "An infusible end-product resins which showed incomparably better dielectric properties than what we obtain in making a material by means of dry phenol and dry hexamethylenetetramine as described by Dr. Redman and his collaborators."

Just how a material can be at one and the same time equal to itself and incomparably better than itself would seem to call for explanation.

It has been no part of our purpose to engage in controversy with a gentleman who has shown untiring industry in studying the work of the earlier inventors and putting to industrial uses the results of their labors supplemented by his own discoveries. Our effort, in our earlier paper, was to set forth something of the history of the art of producing synthetic resins, and it did not occur to us that in so doing we should give offense to our highly esteemed contemporary or furnish the animus for Dr. Baekeland's criticism to which we have here made reply.

L. V. REDMAN

A. J. WEITH

F. P. BROCK

AMBERIOD CHEMICAL PRODUCTS CO.  
636-678 WEST 22ND ST. CHICAGO  
February 16, 1914

### VALUATION OF FLUORSPAR

*Editor of the Journal of Industrial and Engineering Chemistry:*

In THIS JOURNAL, 4, 201 and 548, I published a quick method for the determination of the principal constituents of Fluorspar. This method is now used in our mine laboratory and has proved very satisfactory. In practical work, I have made some slight modifications, increasing thereby the accuracy of the results, so I believe the modifications may be of interest to some of my colleagues.

After dissolving the carbonates by diluted acetic acid, I evaporate to dryness, add 50 cc. water and heat to boiling to precipi-

itate the iron, dissolved by acetic acid, as basic acetate. Thereby the small amount of iron soluble in acetic acid is not calculated in the amount of calcium carbonate, as it would be by filtering off the acetic acid solution. Furthermore, the amount of calcium fluoride brought in solution is smaller, since the solubility of calcium fluoride in acetic acid is higher than in water: 50 cc. hot water dissolve 0.8 mg. calcium fluoride, while 50 cc. acetic acid (1:10) dissolve 10 mg. of calcium fluoride.

After volatilizing the silica, I decompose the metal oxides, as formerly, by digesting and evaporating the residue with hydrofluoric acid and a few drops of nitric acid. By this operation under certain conditions, some calcium nitrate can be formed and left undecomposed, which would cause an error because of the solubility of calcium hydroxide in the alkaline extraction solution. Also in fluorspar high in iron, some iron nitrate can be left undecomposed, which will change to a basic salt by evaporating, which basic salt is insoluble in the extraction solution.

Therefore, I repeat the evaporation with hydrofluoric acid in all cases in order to be sure that all nitrates are transformed into fluorides. Investigating the action of nitric acid on calcium fluoride, I evaporated one gram of pure crystallized fluorspar, finely ground, with different amounts of nitric acid and calculated the amount of decomposed Calcium Fluoride from the increase of weight as follows:

G. CaF <sub>2</sub>	Cc. HNO <sub>3</sub> Sp. gr. 1.42	G. CaF <sub>2</sub> decomposed
1	0.5	0.0034
1	1.0	0.0057
1	1.5	0.0089
1	2.0	0.0114
1	2.5	0.0131
1	3.0	0.0163

By digesting and evaporating these residues with 2 cc. hydrofluoric acid (50 per cent), I obtained the original weight of one gram fluorspar, showing that one evaporation with 2 cc. 50 per cent hydrofluoric acid is sufficient to decompose the calcium nitrate formed by evaporating one gram fluorspar with 3 cc. nitric acid (1.42).

Considering these results, I changed the method as follows: After volatilizing the silica and weighing the residue add 2 cc. hydrofluoric acid and 10 drops of nitric acid, cover the crucible with its lid and place on a moderately warm water bath thirty minutes; then remove the lid and evaporate to dryness, add 2 cc. hydrofluoric acid and evaporate again to dryness, etc., as described in my first paper.

Working in this manner, no calcium salt is dissolved by the extraction solution and only a small amount of calcium fluoride is washed out corresponding to the solubility of calcium fluoride in water.

The corrections I am using in this modified method, taking one gram of Fluorspar for analysis, are:

- (1) For loss in weight by treating with acetic acid, evaporating to dryness and boiling after the addition of 50 cc. water . . . . . 0.0010 g
  - (2) For loss in weight by treating with HgO and HF . . . . . 0.0002 g
  - (3) For loss in weight by treating with ammonium acetate . . . . . 0.0010 g
- 0.0022 g.

E. BIDTEL

LABORATORY FAIRVIEW FLUORSPAR & LEAD CO.  
GOLCONDA, ILLINOIS  
February 2, 1914

### NOTE ON THE ELECTROLYTIC DETERMINATION OF COPPER

*Editor of the Journal of Industrial and Engineering Chemistry:*

In the electrolytic determination of copper from nitric acid solutions the deposit is very bright and adherent, if the correct acidity concentration conditions have been maintained. When the acid concentration is too low the film has a dull look and may

not be adherent. If the acid concentration is too high a long time will be required to completely deposit the metal, although the deposit will be very bright.

In those cases where it is very convenient to limit the amount of free acid in bringing the copper into solution in preparing for the electrolysis, and where the results of the analysis are needed in the shortest possible time for control work, this excess acidity can be very easily controlled by the addition of a little powdered sodium acetate to the solution.

In preparing the solution for electrolysis all the nitric acid can be used that is necessary to quickly bring into solution the copper, copper salts, or compounds containing copper. Then after the electrodes have been mounted, the current switched on, and current density adjusted, if the copper does not promptly start to plate out, a little sodium acetate dusted into the solution will fix the excess of nitric acid which is dissolving the copper film as fast as formed.

The change in the character and speed of deposition will be almost instantaneous and the deposit will be bright, adherent, and formed in the minimum of time. The treatment of the solution with an excess of sodium acetate at the end of a deposition in order to change the free nitric acid to sodium nitrate and thus enable the electrodes to be removed without previous washing has been recommended often and the action is the same in both cases, differing only in degree.

H. CLOUKEY

FOREST PRODUCTS LABORATORY  
MADISON, WISCONSIN  
December 27, 1913

#### REMARKS ON WHITE LEAD PAINT PUBLISHED IN 1810

*Editor of the Journal of Industrial and Engineering Chemistry:*

Mr. Frederick L. Hoffman, Statistician of the Prudential Insurance Company of America, has kindly sent me for perusal a rare volume of the *Memoirs of the Connecticut Academy of Arts and Sciences*, published in New Haven in 1810. On pages 135 and 136 occurs a letter from N. Webster, Jr., to Mr. Benjamin Silliman, Secretary of the Academy. I enclose a copy of this letter, thinking perhaps it might be interesting to the readers of the JOURNAL. It is interesting no note that in those days they spoke of the "new chemistry" in pretty much the same way that we do to-day. The "new chemistry" of Webster, however, is not very new now.

G. W. THOMPSON

129 YORK ST., BROOKLYN  
January 27, 1914

#### ON THE DECOMPOSITION OF WHITE LEAD PAINT

*To Mr. BENJAMIN SILLIMAN, Secretary of the Connecticut Academy of Arts and Sciences.*

SIR,

It is well known, that a white paint, formed by mixing oil, and usually vegetable oil, with the white oxyd of lead, is very expensive, and not very durable. Within a few years after this paint is laid upon a building, it is observed that the oil has been separated from the lead, and the latter may be rubbed off with the hand, being reduced to a state in which it is easily pulverized. It is observable also, that the like paint on inside work, not exposed to water, is not liable to the same change. From these facts, it is probable that the oil, when exposed to water, undergoes a slow decomposition.

Oil is proved, by chemical analysis, to be composed of carbon, or pure charcoal, and hydrogen, or the base of inflammable air, in the proportion of nearly four parts of the former, with one of the latter. Now carbon has a very strong affinity for oxygen, one of the constituent elements of water. Is it not probable that the decomposition of the oil of paints is owing to that affinity—the carbon of the oil combining with the oxygen of water, and the hydrogen of the oil, being set free, escaping in the form

of gas? If so, the art of rendering the paint durable will consist in fixing the oil, or preventing this decomposition. This is undoubtedly a great desideratum in the arts. In the course of my scanty reading on subjects of this kind, I have found nothing satisfactory. The experiments of M. de Morveau, as related in a paper communicated to the Academy of Dijon, of which an extract is found in the Encyclopedia, were evidently made before the date of the new Chemistry. It is believed that the causes of the changes which paints undergo, and which he ascribes to phlogistic vapors, are now better understood than when he wrote; and it is desirable that the attention of the chemist, as well as the artist, may be invited to the subject.

If the funds of the Academy would permit, it might be well to offer a premium for the discovery of a substance which should fix the oil in white paints, without changing their color.

I am, Sir, respectfully, your obedient servant,

N. WEBSTER, JUN.

New-Haven, Oct. 30, 1804

#### FORTY-NINTH MEETING OF THE AMERICAN CHEMICAL SOCIETY, CINCINNATI, APRIL 7-10, 1914

A meeting of the American Chemical Society will be held in Cincinnati, Ohio, April 7th to 10th, inclusive, the beginning date having been changed from April 8th to April 7th since the announcement in the February Journal. A meeting of the Council will be held at the Hotel Sinton, at eight o'clock, P.M., on Monday evening, April 6th. The meetings of the Society will be held at the University of Cincinnati. The Hotel Sinton on the corner of Fourth and Vine Streets has been chosen as headquarters. Other hotels will be designated in the final program, which will be sent to all members who signify their intention of attending the meeting.

The following committees have been chosen to arrange the spring meeting:

F. W. Weissmann, *Chairman*.  
Stephen J. Hauser, *Secretary*. Archibald Campbell, *Treasurer*.  
CHAIRMAN OF SUB-COMMITTEES  
C. Farnham, *Transportation and Excursions*.  
C. T. P. Fennel, *Publicity, Press and Printing*.  
J. W. Ellms, *Reception*.  
John Uri Lloyd, *Meeting Places*.  
Mrs. J. W. Ellms, *Ladies' Reception*.  
Richard Lord, *Entertainment*.  
Lauder W. Jones, *Banquet*.  
F. C. Brocman, *Snoozer*.  
Archibald Campbell, *Finance*.  
F. O. Clements, *Reception at Dayton, O.*

All Divisions of the Society will meet, and the Water, Sewage, and Sanitation Section have announced that they are planning a special conference on Standard Methods of Water Analysis. As Cincinnati is near to some of our largest rubber manufacturing centers a large meeting of the Rubber Section is expected.

The Secretary of the Local Section announces the following detail:

"The Entertainment Committee is planning many interesting events, and special preparations are being made to provide entertainment for ladies, who may attend, at times when they cannot participate in the regular meetings. One particularly interesting feature will be the concert given by the Cincinnati Symphony Orchestra, under the direction of Ernst Kunwald, which has been arranged for Wednesday evening.

"The Transportation Committee has arranged a number of interesting visits to local industrial plants. It is a well known fact that Cincinnati has a very large variety of industries which are strictly chemical or very closely allied. This Committee has already arranged trips to the Filtration Plant, Proctor and Gamble's, the home of Crisco, Globe Soap Co., Diamalt Co., Andrew Steel Works, Boldt Glass Co., the New Cincinnati Hospital, the largest and most modern city hospital in the

world, Machine Tool Plants, Rookwood Pottery, Lloyd Brothers, W. S. Merrill Chemical Co. and many others.

"In addition to these inspection trips, the Committee is planning to devote Friday, April 10th, to visit adjacent industrial plants, an all day excursion. It is planned to go to Middletown during the morning and inspect the plant of the American Rolling Mills, the home of Ingot Iron. After visiting this plant, we shall go to Dayton, where members of the Cincinnati Section, residents of Dayton, have arranged an inspection trip through the plant of the National Cash Register Co. Negotiations are now in progress to have Mr. Wright give an exhibition of his latest Aeroplane, including the stabilizer.

"The following provisional program will give an idea of the plans for the Cincinnati meeting.

MONDAY,	Apr. 6,	Evening, Council Meeting
TUESDAY,	Apr. 7,	Morning, General Meeting Afternoon, Excursions Evening, Smoker at Zoo
WEDNESDAY,	Apr. 8,	Morning, Division Meetings Afternoon, Excursions Evening, Concert by the Cincinnati Symphony Orchestra at Emery Hall
THURSDAY,	Apr. 9,	Morning, Division Meetings Afternoon, Excursions Evening, Subscription Dinner
FRIDAY,	Apr. 10,	Excursion to American Rolling Mills, Middletown; to National Cash Register Co., Dayton."

All titles for papers should be in the Secretary's hands on or before March 23rd, or in the hands of the Secretaries of Divisions by March 21st, in order to be placed on the final program. By vote of the Council no papers can be presented at the meeting that are not printed on the final program.

#### ADDRESSES OF SECRETARIES

##### DIVISIONS

*Agricultural and Food Chemistry*, Glen F. Mason, H. J. Heinz Company, Pittsburgh, Pa.

*Biological Chemistry*, I. K. Phelps, Bureau of Chemistry, Washington, D. C.

*Fertilizer Chemistry*, F. B. Carpenter, Virginia-Carolina Chemical Co., Richmond, Va.

*Industrial Chemists and Chemical Engineers*, S. H. Salisbury, Jr., Lehigh University, South Bethlehem, Pa.

*Organic Chemistry*, C. G. Derick, Morris Ave., Lincoln Place, Urbana, Ill.

*Pharmaceutical Chemistry*, A. P. Sy, University of Buffalo, 24 High St., Buffalo, New York.

*Physical and Inorganic Chemistry*, R. C. Wells, U. S. Geological Survey, Washington, D. C.

##### SECTIONS

*India Rubber Chemistry*, Dorris Whipple, The Safety Insulated Wire and Cable Co., Bayonne, N. J.

*Water, Sewage and Sanitation*, Harry P. Corson, State Water Survey, Urbana, Ill.

The final program will be sent to all members of the Cincinnati Section, to Secretaries of Local Sections, to members of the Council and to all members requesting same. The expense of printing and mailing this program is so great that it is sent only to those who especially desire it on account of their intention of attending the meeting. Other members will find it printed in the Society's Journals.

Cincinnati is centrally located, and is accordingly easily reached by all members of the Society. Every member of the Society should make an effort to be present, for it is hoped and expected that this will be the largest meeting of the American Chemical Society ever held in the spring.

CHARLES L. PARSONS, *Secretary*

Box 505, WASHINGTON, D. C.

February 19, 1914

#### NOTE ON CERTAIN UNPUBLISHED WORK ON ELECTROLYSIS USING SUPPORTED MERCURY KATHODE—A CORRECTION

In THIS JOURNAL, 6, 166 my name was omitted as author of the article under the above title.

ERNEST A. LESUEUR

OTTAWA, ONTARIO

## PERSONAL NOTES

The program of the first public meeting of the Radium Institute of America, held at Columbia University on Feb. 17th, was as follows: "Introductory Remarks," Pres. N. M. Butler; "The Experiment of Counting the Alpha Particles," Prof. Geo. B. Pegram; "Some Experiments with Radium Emanation," Prof. William Duane; "Therapeutic Use of Radium," Dr. Robert Abbe; "Some Biological Effects from Radium," Prof. Francis Carter Wood.

Dr. Wolfgang Ostwald, of the University of Leipzig, Germany, was the guest of honor at a dinner given by the Cincinnati section of the A. C. S. and the Cincinnati Research Society, at the Business Men's Club, on Feb. 11, 1914.

Dr. F. K. Cameron, of the Bureau of Soils, spoke before the Washington Section of the A. C. S. on Feb. 12, 1914. Dr. Cameron gave an illustrated lecture on "Potash from Kelp."

Prof. Harry C. Jones, of Johns Hopkins University, gave an illustrated lecture on "The New Era in Chemistry," before the Philadelphia Section of the A. C. S. on Feb. 21, 1914.

The Michigan Section of the A. C. S. met Jan. 22, 1914 and were addressed by Mr. W. L. Badger on "The Work of the Bureau of Standards."

Mr. Wm. H. Blauvelt, Consulting Engineer of the Smet-Solvay Co., Syracuse, N. Y., gave an illustrated lecture on "By-Product Coke Ovens from the Chemical, Engineering and Economic Standpoints," before the Pittsburgh Section of the A. C. S., Feb. 19, 1914.

Prof. W. P. Mason, of the Rensselaer Polytechnic Institute at Troy, N. Y., lectured on Jan. 29th before the Franklin Insti-

tute of Philadelphia on "Advantages and Disadvantages of Water Storage."

Dr. Walter P. Bradley has resigned as Professor of Chemistry after twenty-five years of service at Wesleyan University to take charge of the investigations of the United States Rubber Company in whose employ he recently spent a year's leave of absence.

The University of Illinois offered a two weeks' course on "The Technology of the Clay Industries," from Jan. 12th-24th, under the direction of Mr. A. V. Bleining, of the Bureau of Standards at Pittsburgh, and Mr. R. T. Stull, Acting Director, Ceramics Department, University of Illinois. This course was intended for men actively engaged in the industries and an attempt was made to apply the chemical and physical principles underlying the operations of preparation, shaping, drying, burning and decorating. Additional subjects, such as Construction of Furnaces and Kilns, Power Plants, Power Transmission, Dynamos and Motors, Care of Machinery, etc., were presented. The engineering topics were treated by Acting Dean Richards, of the Mechanical Engineering Department and his associates. For the complete course, 51 men registered and a smaller number attended for a shorter time. All of these men are connected with the ceramic industries in the capacity of managers, superintendents or in charge of plant departments.

Mr. C. H. Teesdale, of the Forest Products Laboratory, Madison, Wisconsin, will address the Chicago Section of the



A. C. S. at the March meeting on his special work on Wood Preservation.

Mr. J. Lanison Wills, F.C.S., of the Stifel Laboratory of Fermentology, addressed the Feb. 9th meeting of the St. Louis Section of the A. C. S. on "American Beer from the Chemical and Biological Viewpoint."

Mr. W. D. Richardson, Chief Chemist of Swift & Co., Chicago, addressed the Detroit Chemists on Jan. 30th, his subject being "The History and Present Status of Food Preservation."

Walter Wallace Weir has been placed in charge of cooperative drainage experiments being carried on at Kearney Park, near Fresno, on the 5,400-acre ranch belonging to the University of California. The University and the Office of Experiment Stations of the U. S. Dept. of Agric. are making these investigations in the reclamation of alkali lands by drainage ditches and a pumping system.

The Nashville Section of the A. C. S. was addressed on Feb. 20, 1914, by Mr. E. J. Pranke, who spoke on "Some Problems of the Cyanamid Industry and their Industrial Solution."

Mr. Paul Poetschke has resigned from the position of Assistant Director of the Department of Chemistry of the Lederle Laboratories, New York, after ten years of continuous service with that company; he was presented with a beautifully inscribed loving cup by the officers, employees and friends associated with the Lederle Laboratories and Lederle & Provost. Mr. Poetschke's present position is that of Director of the Department of Chemistry of the L. D. Caulk Co., Milford, Del., manufacturers of dental materials: his new work will be in connection with various lines of research leading to scientific development and application of the materials used in dentistry, as well as improvements in processes of manufacture and the standardization of materials.

Mr. Frank A. Ladbury, Works Manager of the Olbury Electro-Chemical Co., of Niagara Falls, gave an experimentally illustrated address before the Rochester Section of the A. C. S.,

Feb. 2, 1914, on "Some Aspects of the Electro-Chemical Industry."

Mr. Lewis J. Seidensticker, formerly with the Warner Sugar Refining Co., Edgewater, N. J., has accepted the position of Manager of the Atlantic Sugar Refineries, Ltd., St. John, N. B., Canada.

Prof. A. H. Blanchard, in charge of the graduate course in highway engineering at Columbia University, delivered illustrated lectures on Jan. 26th at the University of Illinois, his subjects being: "Bituminous Surfaces and Bituminous Pavements," and "Modern Developments in Highway Engineering in Europe."

The Food and Drug Inspection work of the Bureau of Chemistry has been reorganized, the country being divided into three districts, each under a District Chief, who will be in charge of the branch laboratories and the work of the inspectors in his territory. It is expected that the Pittsburgh, Kansas City, Nashville, Portland and Omaha Laboratories will be closed by April 1st. The Eastern District, in charge of Mr. W. G. Campbell (now Chief Inspector) with headquarters at the Bureau in Washington, includes the laboratories at New York, Boston, Philadelphia, Buffalo, Pittsburgh, Savannah and San Juan. The Central District under Mr. L. M. Tolman (now Chief of the Washington, D. C., Food Inspection Division) takes in the laboratories at Chicago, St. Paul, St. Louis, Cincinnati, New Orleans, Nashville, Kansas City and Omaha. The Western District, in charge of Mr. B. R. Hart (formerly of the Cincinnati Laboratory) with headquarters at San Francisco, includes the territory west of the Rocky Mountains and the branch laboratories at San Francisco, Denver, Portland, Seattle and Honolulu.

Dr. Robert Kennedy Duncan, Director of the Mellon Institute of Industrial Research of the University of Pittsburgh, died at his home in Pittsburgh on February 18, 1914, after an illness of several weeks.

## BOOK REVIEWS

**Treatise on General and Industrial Organic Chemistry.** By DR. ETTORE MOLINARI. Translated from the second, enlarged and revised Italian edition by Thomas H. Pope. Philadelphia: P. Blakiston's Son & Co., 1913. Pp. xix + 770. 506 illustrations. \$6.00 net.

There are plenty of excellent modern textbooks on general organic chemistry already on the market and new ones are constantly appearing. There are also many admirable standard works on industrial organic chemistry and this number also is being steadily increased. It would therefore seem a rather difficult matter to find any places in the field not already fully occupied, or any need not already satisfactorily met. Yet, in the opinion of the reviewer, Dr. Molinari has found one of these few remaining uncrowded parts of the field and his book therefore meets a need not heretofore properly provided for. Mr. Pope has done a service to all English-speaking chemists in translating it into our own tongue. The recording of weights in quintals throughout the book will look more familiar to the Englishman than to the American.

In textbooks on general organic chemistry there is usually only an occasional brief reference to the industrial importance of the compound or reaction discussed, practically all of the space being given up to a consideration of the theoretical side of the subject. Similarly, the textbooks on industrial organic chemistry as a rule give but scant attention to the theoretical questions involved or attempt to arrange their material with regard to its proper place in a scientific classification of the whole field, the arrangement being almost without exception from the standpoint of the industrialist and not from that of the teacher. There

is thus a gap between the two, and it is just this gap which Dr. Molinari has endeavored to bridge.

His book is essentially a textbook of general organic chemistry, in which all groups of organic compounds are classified as usual according to their structural formulas, and with which has been incorporated and properly distributed under this classification a textbook of industrial organic chemistry. In other words, the problem was to take a book like Sadtler's "Industrial Organic Chemistry" and add this material, in the proper places, to that already given in such a book as Berntsen's "Organic Chemistry." The result of such a fusion is, as just pointed out, a textbook of general organic chemistry with special emphasis on and detailed treatment of its industrial side. Such an arrangement is of advantage both to the student of general chemistry and to the industrialist. To the former, it points out at once which are the compounds and reactions of commercial importance, what their significance is to the community, and what are the actual manufacturing processes by which they are produced. On the other hand, it teaches the industrialist the place of his own special line of manufacturing in the whole wide field of organic chemistry, what other compounds and reactions are most closely related to those which occupy his chief attention, and gives him a clearer insight into the importance of the underlying theoretical principles.

It will be admitted at the outset that it is not an easy problem to condense two such textbooks into one volume of convenient size. It was necessary, naturally, to sacrifice something of each, to keep down the size of the volume, but on the whole the work has been well done, and its author is to be congratulated. Where

the trimming can be done with least injury in such a consolidation is a matter of opinion and will, of course, be decided by the viewpoint of the author. On the industrial side, it may be determined solely on the basis of the commercial importance of the subject or, on the other hand, the determining factor may be the extent to which chemistry enters into the processes involved. Personally, in a book of this kind, the reviewer, being a teacher, would like to see the latter the chief factor in deciding the question; more space being given to such matters as synthetic drugs and synthetic perfumes and less to sugar, textiles and the like, where the engineering features are so much more in evidence than the chemical. Where various methods are given for the manufacture of the same products, an indication of the relative commercial importance of each should be given, so that the reader may be able to pick out at a glance the leading present-day practice.

It is scarcely to be expected that a book of this size and scope should be wholly free from minor defects, and the rigorous critic who goes over it with a fine-tooth comb will discover here and there statements which are inaccurate or misleading. These occasional lapses presumably will be corrected in subsequent editions.

An immense amount of labor has been expended in gathering and properly distributing the mass of material contained in the volume. Much statistical information is included and constitutes a very valuable feature. References and special bibliographies are, however, generally lacking; and it is to be hoped that the author can include them in future editions. In fact, the reviewer would be glad to see the scope of the work enlarged, even though it involved the publication of two volumes instead of one.

The book is a welcome addition to the literature of the subject, and is just what is wanted in courses in organic chemistry for engineering students, especially for those intending to become chemical engineers.

**Part I. General.** This part comprises the usual introduction to textbooks of organic chemistry and deals with such topics as the purification and analysis of organic compounds, determination of empiric, molecular, constitutional and stereochemical formulas, valency, isomerism, polymerism, homology and isology, the bearing of chemical composition and constitution upon physical properties, classification of carbon compounds, official nomenclature and the like. It would seem desirable to add here also some facts of special interest to the future chemical engineer concerning chemical manufacturing processes in general, the most important factors governing industrial operations, standard forms of apparatus, the difference between test tube reactions and those of the plant, and the like; material similar in character to that contained in the recent address of O. N. Witt, before the general meeting in Prague of the Austrian Union for the Advancement of Chemical Industry, on the methods of work of the chemical laboratory and of chemical industry and their inter-relations.

**Part II. Derivatives of Methane.** A discussion of the more important groups of straight-chain carbon compounds. The classification employed in this part does not appeal to the reviewer as logical or as the best adapted to the purposes of the author. It seems unfortunate, for example, to discuss acetic acid and its salts in one part of the book (p. 270), acetic anhydride in another part (p. 320), and the esters of acetic in still a third place (p. 371); and not to consider the industries of the oils, fats, waxes, candles and soaps, in closer connection with the corresponding fatty acids. In addition to the industries just mentioned, this part contains a discussion also of the following: gas, petroleum, alcohol and alcoholic beverages, explosives, tartaric acid, citric acid, sugar, starch and paper, as well as many others (wood distillation, vinegar, glycerol, glucose, etc.) treated more briefly.

**Part III. Cyclic Compounds.** A discussion of the more important groups of cyclic carbon compounds. This includes descriptions of the following industries: coal tar, tanning, coloring matters, textile fibres; also briefer articles on synthetic

perfumes, synthetic drugs, synthetic rubber, etc., several of which merit fuller treatment.

M. T. BOGERT

**Preservative Coatings for Structural Materials.** Reports of Committee D-1 of the American Society for Testing Materials, 1903-1913. Edited by the Secretary and published by the Society. Philadelphia. 431 pages. Quarto. Cloth. Price, \$2.00.

The study of protective coatings for iron and steel, begun by the American Society for Testing Materials in 1903 and continued unbrokenly and with increasing effectiveness to the present time, is described in detail in these reports, now published in combined form in a single volume.

During the first few years the Committee planned its investigations and formulated its standards but as soon as definite lines became clear, the work was taken up and pushed as vigorously as possible, consistent with the exercise of conservative judgment.

The first constructive work the Committee undertook was in the application of nineteen different paints on the Havre de Grace Bridge in 1906. Since then a great deal has been accomplished in the study of white paints, the influence of pigments upon corrosion, linseed oil, soya bean oil, China wood oil, turpentine, definitions of terms used in paint specifications, etc. There is probably no book which contains within its covers so much original work on the subject of paints.

The Committee, made up, half of representatives of producing interests, and half of representatives of consuming interests, constitutes a body of investigators, unhampered as to any line of investigation, but conservative as to the conclusions it draws.

The volume is arranged chronologically, and the contents give full information as to where the reports of the various subcommittees appear. These reports contain numerous tables giving analyses and classifications of paint materials unobtainable elsewhere. The volume is well printed and paged both with respect to the annual reports and serially for this volume only. All persons interested in paint technology will find much valuable material in this book.

**Die Gerbstoffe-Botanische-chemische Monographie der Tannide.**

By J. DEKKER. Borntraeger, Berlin. Translated to the German from the Dutch, by Otto Klipp. 586 pp. Price, \$5.25.

The first synthetic tanning agent was prepared in 1912 and the next few years will undoubtedly see tremendous progress in this field, not only in our at present limited chemical knowledge, but also in the better control and understanding of their technical application.

The author has carried out the work so well that a brief description of the arrangement of the subject matter is all that is required.

The book is divided into two parts: Part I treating the Bibliography and Botany, and Part II dealing with the Chemistry of the Tannins.

Part I is divided into three chapters: Chapter I, Bibliography, Journals and Books, 1754-1913; Chapter II, Distribution of the Tannins in the Various Plants; Chapter III, (1) Analytical Methods of Identification; (2) Distribution of the Tanning Agents in the Plant; (3) Significance of the Tanning Agents to the Life of the Plant.

Part II, dealing with the strictly chemical side of the tanning agent, is divided into four chapters: Chapter I, Tannin and Tannin-Like Substances; Chapter II, Chemistry of the Tanning Agent; Chapter III, Analytical Methods; Chapter IV, Technical Applications of the Tanning Agents.

The author has produced a splendid book which brings together the available botanical and chemical knowledge of the tannins, which will be appreciated by all interested in either the scientific or technical application of the tanning agents.

OTTO KRESS

# NEW PUBLICATIONS

By D. D. BEROLZHEIMER, Librarian The Chemists' Club, New York

- Analysis, Gas, Exercises in.** By HARTWIG FRANZEN. 12mo. 120 pp. Price, \$1.00. Blackie & Son, London. (Translation in English.)
- Asphalts, Natural and Artificial, Chemistry and Technology of the.** By H. KOEHLER and E. GRAEFE. 2nd Ed. 8vo. Price, \$4.75. Friedrich Vieweg & Sohn, Brunswick. (German.)
- Atoms, The.** By JEAN PERRIN. 8vo. 190 pp. Price, \$1.50. Theodor Steinkopff, Dresden. (Translation in German.)
- Constitution, Chemical, and Physical Properties.** By S. SMILES. 8vo. 688 pp. Price, \$5.25. Theodor Steinkopff, Dresden. (Translation in German.)
- Cyanogen Compounds, The Industry of the.** By H. KOEHLER. 8vo. Price, \$1.75. Friedrich Vieweg & Sohn, Brunswick. (German.)
- Electric Furnace, The.** By ALFRED A. STANSFIELD. 2nd Ed. 8vo. 415 pp. Price, \$4.00. McGraw-Hill Book Co., New York.
- Explosives, Permissible, Tests of.** By CLARENCE HALL and SPENCER P. HOWELL. 8vo. 313 pp. U. S. Bureau of Mines, Bulletin 66.
- Inorganic Chemistry, New Views in the Domain of.** By A. WERNER. 3rd ed. 8vo. 419 pp. Price, \$3.00. Friedrich Vieweg & Sohn, Brunswick. (German.)
- Iron and Steel Production, Electrothermal, Methods of.** By J. B. C. KERSHAW. 8vo. 264 pp. Price, \$2.25. Constable & Co., London.
- Mechanics, Technical.** By EDWARD R. MAURER. 3rd Ed. 8vo. 343 pp. Price, \$2.50. John Wiley & Sons, New York.
- Metals, Precious, The Sampling and Assay of the.** By E. A. SMITH. 8vo. 476 pp. Price, \$4.00. Chas. Griffin & Co., London.
- Metallurgy, General.** By H. O. HOFMAN. 8vo. 909 pp. Price, \$6.00. McGraw-Hill Book Co., New York.
- Nickel and Cobalt, Methods of Determination of, and Separation from Other Elements.** By H. GROSSMANN. 8vo. Price, \$1.25. Ferdinand Enke, Stuttgart. (German.)
- Paint Making and Color Grinding.** By CHARLES L. UEBELE. 8vo. 483 pp. Price, \$10.00. Painters Magazine, New York.
- Petroleum: Oil Production Methods.** By PAUL M. PAINE and B. K. STROUD. 8vo. 240 pp. Price, \$3.00. Western Engineering Publishing Co., San Francisco.
- Poisoning, Industrial, from Fumes, Gases, and Poisons of Manufacturing Processes.** By J. RAMBOUSEK. 8vo. 360 pp. Price, \$3.50. Longmans, Green & Co., New York. (Translation in English.)
- Potash Industry, Trade Effluents from the, their Removal and their Effect in and on Water Mains.** By J. H. VOGEL. 8vo. Price, \$7.00. Gebrauder Borntraeger, Berlin. (German.)
- Pyrotechnics.** By VANNOCIO BIRINGUCCIO, A. MIELI and E. TROILLO. 8vo. 198 pp. Società Tipografica, Bari (Italy). (Italian.)
- Radium Report.** By MR. FOSTER. 63rd Congress, 2nd Session, House of Representatives, Report No. 217. 18 pp.
- Rubber, The Chemistry of.** By B. D. PORRITT. Cr. 8vo. 96 pp. Price, \$0.50. Gurney & Jackson, London.
- Rubber, Plantation, The Preparation of.** By SIDNEY MORGAN. Roy. 8vo. 269 pp. Price, \$2.75. Rubber Growers' Association, London.
- Rubber and Rubber Planting.** By R. H. LOCKE. Cr. 8vo. 245 pp. Price, \$1.50. Cambridge University Press, Cambridge.
- Tannins, The.** By J. DEKKER. 8vo. 586 pp. Price, \$5.00. Gebrauder Borntraeger, Berlin. (German.)
- Technical Processes and Manufacturing Methods, The Application of Physico-Chemical Theory to.** By R. KREMANN. 8vo. 212 pp. Price, \$3.00. D. Van Nostrand Co., New York. (Translation in English.)
- Thermodynamics, A Textbook of.** By JAMES RIDDICK PARTINGTON. 8vo. 544 pp. Price, \$4.00. D. Van Nostrand Co., New York.
- Water Purification, Modern Methods of.** By J. DON and J. CHISHOLM. 2nd Ed. 8vo. 416 pp. Price, \$4.00. E. Arnold, London.
- Yearbook of Chemistry for 1912.** By RICHARD MEYER. 22nd Ed. 8vo. 577 pp. Price, \$5.00. Friedrich Vieweg & Sohn, Brunswick. (German.)
- Ammonia, Inorganic, Syntheses of.** By O. SERPEK. *Zeitschrift fuer angewandte Chemie*, Vol. 27, 1914, No. 8, pp. 41-48.
- Benzol of Commerce, Determination of the Total Sulfur in.** By KONRAD SCHENK. *Chemiker Zeitung*, Vol. 38, 1914, No. 8, pp. 83-84.
- Bromin, An Apparatus for the Manufacture of.** By KONRAD KUHNESCHY. *Chemische Apparatur*, Vol. 1, 1914, No. 1, pp. 20-25.
- Carbohydrates, The Picrate Colorimetric Method for the Estimation of.** By WILLIAM M. DEHN and FRANK A. HARTMAN. *Journal of the American Chemical Society*, Vol. 36, 1914, No. 2, pp. 403-409.
- Chemical Industry, Modern** (Hurter Memorial Lecture). By FRITZ HABER. *Journal of the Society of Chemical Industry*, Vol. 33, 1914, No. 2, pp. 49-54.
- Coal, Bituminous, Natural Gasification of.** By ERNST SCHMATOLLA. *Chemiker Zeitung*, Vol. 38, 1914, No. 6, pp. 61-63.
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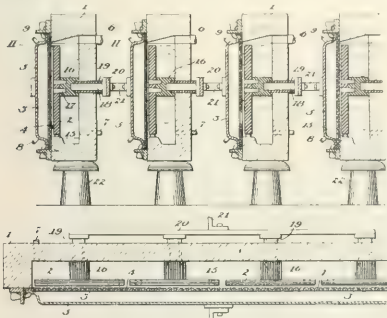
## RECENT JOURNAL ARTICLES



# RECENT INVENTIONS

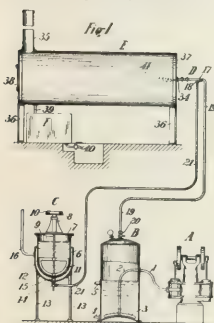
By C. L. PARKER, Solicitor of Chemical Patents, McGill Building, Washington, D. C.

**Electrolytic Cell.** C. W. Marsh, Oct. 14, 1913. U. S. Pat. 1,075,362. The cell is of the diaphragm type intended for the decomposition of sodium and potassium chlorides. The anode



compartment is open at one side only. A substantially vertical pervious cathode and diaphragm is disposed across the opening and an anode connection extends horizontally through the wall of the cell opposite the electrode.

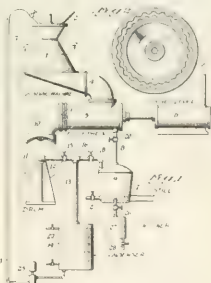
**Restoring Coagulated Albumins to the Original State.** A. H. Rasche, Oct. 21, 1913. U. S. Pat. 1,076,232. The liquid or emulsion containing the coagulated albumins is first heated, agitated and supersaturated with a compressed chemically indifferent gas. The treated material is then atomized by means of the chemically indifferent gas into an open vessel.



**Art of Forming Chemical Compounds.** T. A. Edison, Jan. 6, 1914. U. S. Pat. 1,083,355. Nickel hydroxid for use in storage batteries is produced by mixing intimately a dry pulverized salt

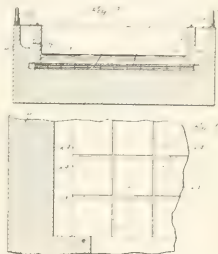
of nickel containing water of crystallization and an excess of dry soluble hydroxid. The resulting mixture is dried, crushed, washed, and the residue, nickel hydroxid, dried.

**Extracting Oils and Fats from Oil-Seeds, Etc.** R. N. Riddle, Oct. 28, 1913. U. S. Pat. 1,076,997. The oil-containing materials are subjected to alternate crushing pressure and release of pressure while subjecting them to the action of the solvent. The alternate pressure and release of pressure are obtained by the action of the corrugated surfaces of the grinding mill.



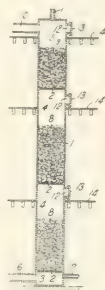
**Gunpowder and Process of making the same.** C. D. McDowell, Jan. 6, 1914. U. S. Pat. 1,083,371. The composition comprises eight ounces of potassium chlorate, seven ounces of granulated sugar, one drachm of glycerin and two drachms of water.

**Chemical Filter.** C. S. Bradley, Oct. 28, 1913. U. S. Pat. 1,077,037. Upon the foundation to are laid filter bricks forming a continuous flat outer surface. Within the bricks are formed passages to communicate from one brick to another, whereby pressure and suction are sustained upwardly and downwardly, thereby avoiding displacing tendencies.



**Obtaining Aluminum.** P. C. McIlhiney, Jan. 6, 1914. U. S. Pat. 1,083,691. Aluminum bearing silicious material is treated with hydrofluoric acid to produce aluminum fluorid. The aluminum fluorid is then electrolyzed to obtain metallic aluminum and hydrofluoric acid.

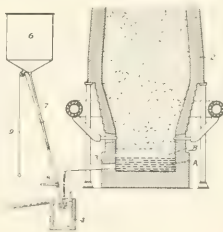
**Recovering Escaping Acid-Gases from Sulfite-Towers.** J. A. DeCew, Oct. 28, 1913. U. S. Pat. 1,077,243. The escaping gases are passed successively through chambers 4, containing moistened limestone and chamber 5 containing moistened magnesite in lump form. It is stated that the use of magnesite saves the 10% to 20% of the sulfur dioxide heretofore lost.



**Manufacturing Phosphoric Acid.** F. Brunschwig, Jan. 6, 1914. U. S. Pat. 1,083,429. Material containing calcium phosphate is treated with less sulfuric acid than is required to combine with the calcium of the phosphate and the reaction is stopped before the impurities go into solution.

**Making Sugar from Cane.** F. G. P. Leao, Jan. 6, 1914. U. S. Pat. 1,083,545. The sugar cane is finely divided and dried at a temperature below 158° F. The dried cane is then saturated with water to dissolve the saccharine matter and the solution separated from the cane by pressure. The resulting syrup is then evaporated and refined.

**Utilizing Iron Blast Furnace Flue-Dust.** R. Baggaley, Dec. 16, 1913. U. S. Pat. 1,081,921. The flue dust and fines are introduced into molten metal and the mixture subjected to a refining process. It is recommended that the dust and fines be introduced into the vortex 5 produced by the fall of the metal into the vessel 4 to insure the dust and fines being immediately enveloped by the molten metal.



**Production of Fertilizers.** A. Messerschmitt, Jan. 6, 1914. U. S. Pat. 1,083,553. Alkali metals containing silicates are decomposed with lime and the alkali metal compounds partially separated from the mixture by lixiviation. The residue is then treated with nitric acid gas. Caustic lime is then added and the mixture lixiviated and evaporated to dryness.

**Effecting Catalytic Reactions.** Hagemann and Baskerville, Jan. 13, 1914. U. S. Pat. 1,083,930. Catalytic reactions are effected by the employment of catalytic metal in the form of very thin leaves.

# MARKET REPORT

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR THE MONTH OF FEBRUARY, 1914

## ORGANIC CHEMICALS

Acetanilid.....	Lb.	21	@	23
Acetic Acid (28 per cent.).....	C	1 62 1/2	@	1 72 1/2
Acetone (drums).....	Lb.	12	@	13
Alcohol, denatured (180 proof).....	Gal.	35	@	37
Alcohol, grain (188 proof).....	Gal.	2 52	@	2 54
Alcohol, wood (95 per cent).....	Gal.	45	@	47
Amyl Acetate.....	Gal.	1 60	@	1 70
Aniline Oil.....	Lb.	10	@	10 1/2
Benzoic Acid.....	Lb.	23	@	27
Benzol (90 per cent).....	Gal.	23	@	25
Camphor (refined in bulk).....	Lb.	4 1/2	@	45
Carbolic Acid (drums).....	Lb.	8	@	10
Carbon Bisulfide.....	Lb.	60	@	8
Carbon Tetrachloride (drums).....	Lb.	7 1/2	@	7 1/2
Chloroform.....	Lb.	22	@	32
Citric Acid (domestic), crystals.....	Lb.	51	@	52
Dextrine (corn).....	C.	2 62	@	2 83
Dextrine (imported potato).....	Lb.	5	@	6
Ether (U. S. P., 1900).....	Lb.	14	@	20
Formaldehyde.....	Lb.	81	@	91 1/2
Glycerine (dynamite).....	Lb.	20	@	21 1/2
Oxalic Acid.....	Lb.	7 1/2	@	7 1/2
Pyrogallol Acid (bulk).....	Lb.	1 20	@	1 40
Salicylic Acid.....	Lb.	25	@	30
Starch (cassava).....	Lb.	33	@	4
Starch (corn).....	C.	1 94	@	1 60
Starch (potato).....	Lb.	41	@	43 1/2
Starch (rice).....	Lb.	8	@	9
Starch (sago).....	Lb.	2 1/2	@	2 1/2
Starch (wheat).....	Lb.	5 1/2	@	6 1/2
Tannic Acid (commercial).....	Lb.	35	@	36
Tartaric Acid, crystals.....	Lb.	31 1/2	@	31 1/2

## INORGANIC CHEMICALS

Acetate of Lead (brown, broken).....	Lb.	7 1/2	@	7 1/2
Acetate of Lime (gray).....	C	1 75	@	1 80
Alum (lump).....	C	1 75	@	2 00
Aluminum Sulfate (high-grade).....	C	1 25	@	1 75
Ammonium Carbonate, domestic.....	Lb.	8	@	8 1/2
Ammonium Chloride, gray.....	Lb.	8 1/2	@	6 1/2
Aqua Ammonia (drums) 16°.....	Lb.	2 1/2	@	2 1/2
Arsenic, white.....	Lb.	3 1/2	@	3 1/2
Barium Chloride.....	C	1 60	@	1 75
Barium Nitrate.....	Lb.	5	@	5 1/4
Barytes (prime white, foreign).....	Ton	19 00	@	23 50
Bleaching Powder (35 per cent).....	C	1 20	@	1 30
Blue Vitriol.....	Lb.	4 80	@	5 1/4
Borax, crystals (bags).....	Lb.	3 1/2	@	4 1/2
Boric Acid, crystals (powd.).....	Lb.	7	@	7 1/2
Brimstone (crude, domestic).....	Ton	22 00	@	22 50
Bromine, bulk.....	Lb.	30	@	35
Calcium Chloride, fused.....	C	60	@	90
Chalk (light precipitated).....	Lb.	4	@	4 1/2
China Clay (imported).....	Ton	nominal		
Feldspar.....	Ton	8 00	@	12 00
Fuller's Earth, powdered, Foreign.....	Ton	16 00	@	17 00
Green Vitriol (bulk).....	C	55	@	60
Hydrochloric Acid (18°).....	C	1 15	@	1 55
Iodine (resublimed).....	Lb.	3 55	@	3 60
Lead Nitrate.....	Lb.	8 1/2	@	8 1/2
Litharge (American).....	Lb.	5 1/2	@	5 1/2
Lithium Carbonate.....	Lb.	65	@	70
Magnesium Carbonate.....	Lb.	21	@	45
Magnesite "Calcined".....	Ton	28 50	@	29 50
Nitric Acid, 36°.....	Lb.	37 1/2	@	4 1/2
Phosphoric Acid (sp. gr. 1.75).....	Lb.	21	@	25 1/2
Phosphorus.....	Lb.	45	@	1 00
Plaster of Paris.....	Hbl	1 50	@	1 70
Potassium Bichromate, 50°.....	Lb.	6	@	7
Potassium Bromide.....	Lb.	39	@	40
Potassium Carbonate (calcined), 80 @ 85%.....	C	3 20	@	3 25
Potassium Chlorate, crystals.....	Lb.	1	@	7 1/2
Potassium Cyanide (bulk), 98-99%.....	Lb.	16	@	18
Potassium Hydroxide.....	C	4 00	@	4 25
Potassium Iodide (bulk).....	Lb.	9 95	@	3 00
Potassium Nitrate (crude).....	Lb.	1	@	5 1/2
Potassium Permanganate (bulk).....	Lb.	9	@	10
Quicksilver, Flask (75 lbs.).....	Lb.	38 00	@	6
Red Lead (American).....	Lb.	6	@	6
Salt Cake (glass-makers').....	C	85	@	65

Silver Nitrate.....	Oz.	36 1/2	@	38 1/2
Soapstone in bags.....	Ton	10 00	@	12 00
Soda Ash (48 per cent).....	C	67 1/2	@	72 1/2
Sodium Acetate.....	Lb.	3 1/2	@	4 1/2
Sodium Bicarbonate (domestic).....	C.	1 00	@	1 10
Sodium Bicarbonate (English).....	Lb.	24	@	3
Sodium Biehomate.....	Lb.	42	@	4 1/2
Sodium Carbonate (dry).....	C.	60	@	80
Sodium Chlorate.....	Lb.	7 1/2	@	7 1/2
Sodium Hydroxide, 60 per cent.....	C.	1 55	@	1 57 1/2
Sodium Hyposulfite.....	C.	1 30	@	1 60
Sodium Nitrate, 95 per cent, spot.....	C.		@	2 22 1/2
Sodium Silicate (liquid).....	C.	65	@	1 50
Strontium Nitrate.....	Lb.	6 1/4	@	7
Sulfur, Flowers (sublimed).....	C.	2 20	@	2 60
Sulfur, Roll.....	C.	1 85	@	2 15
Sulfuric Acid, 60° B.....	C.	85	@	1 00
Talc (American).....	Ton	15 00	@	20 00
Terra Alba (American), No. 1.....	C.	75	@	80
Tin Bichloride (50°).....	Lb.	12 1/2	@	13 1/2
Tin Oxide.....	Lb.	41	@	43
White Lead (American, dry).....	Lb.	5 1/2	@	5 1/2
Zinc Carbonate.....	Lb.	8 1/2	@	9
Zinc Chloride (granulated).....	Lb.	4 1/2	@	5
Zinc Oxide (American process).....	Lb.	53	@	6 1/2
Zinc Sulfate.....	Lb.	21 1/2	@	3

## OILS, WAXES, ETC.

Beeswax (pure white).....	Lb.	45	@	47
Black Mineral Oil, 29 gravity.....	Gal.	13 1/2	@	14
Castor Oil (No. 3).....	Lb.	8 1/2	@	8 1/2
Ceresin (yellow).....	Lb.	12	@	22
Corn Oil.....	C.	6 45	@	6 50
Cottonseed Oil (crude), f. o. b. mill.....	Gal.	44	@	44 1/2
Cottonseed Oil (p. s. y.).....	Lb.	7	@	7 1/2
Cylinder Oil (light, filtered).....	Gal.	21 1/2	@	32
Japan Wax.....	Lb.	12	@	12 1/2
Lard Oil (prime winter).....	Gal.	93	@	95
Linseed Oil (raw).....	Gal.	50	@	52
Menhaden Oil (crude).....	Gal.	32 1/2	@	36 1/2
Neatsfoot Oil (20°).....	Gal.	96	@	98
Paraffine (crude, 120 & 122 m. p.).....	Lb.	3 1/2	@	3 1/2
Paraffine Oil (high viscosity).....	Gal.	26	@	27
Rosin ("F" grade) (280 lbs.).....	Bbl.	4 50	@	4 55
Rosin Oil (first run).....	Gal.	27	@	28
Shellac, T. N.....	Lb.	19	@	19 1/2
Spermaceti (cake).....	Lb.	30	@	35
Sperm Oil (bleached winter), 38°.....	Gal.	72	@	74
Spindle Oil, No. 200.....	Gal.	17	@	17 1/2
Stearic Acid (double-pressed).....	Lb.	9	@	12
Tallow (acidless).....	Gal.	65	@	66
Tar Oil (distilled).....	Gal.	30	@	31
Turpentine (spirits of).....	Gal.	47 1/2	@	48

## METALS

Aluminum (No. 1 ingots).....	Lb.	18 1/2	@	19
Antimony (Hallet's).....	Lb.	7 1/2	@	7 1/2
Bismuth (New York).....	Lb.	2 05	@	2 10
Bronze powder.....	Lb.	50	@	5 00
Copper (electrolytic).....	Lb.	14 1/2	@	14 1/2
Copper (lake).....	Lb.	14 1/2	@	14 1/2
Lead, N. Y.....	Lb.	4	@	—
Nickel.....	Lb.	50	@	55
Platinum (refined).....	Oz.	43 50	@	44 50
Silver.....	Oz.	57 1/2	@	58
Tin.....	C.	39 87 1/2	@	—
Zinc.....	C	5 35	@	5 40

## FERTILIZER MATERIALS

Ammonium Sulfate.....	C	2 85	@	2 90
Blood, dried.....	Unit	3 45	@	—
Bone, 4 1/2 and 50, ground, raw.....	Ton	29 00	@	30 00
Calcium Nitrate (Norwegian).....	C.	2 05	@	2 10
Castor meal.....	Unit	nominal		
Fish Scrap, domestic, dried.....	Unit	nominal		
Mowrah meal.....	Ton	nominal		
Phosphate, acid, 16 per cent bulk.....	Ton	7 00	@	—
Phosphate rock: f. o. b. mine.....	Ton	2 75	@	3 00
Florida land pebble, 68 per cent.....	Ton	2 80	@	5 50
Tennessee, 70 80 per cent.....	Ton	39 07	@	—
Potassium, "muriate," basis 80 per cent.....	Ton	39 07	@	—
Pyrites, furnace size imported.....	Unit	0 13 1/2	@	—
Tankage, high-grade.....	Unit	3 40	@	10

Modern Chemical Industry . . . . .	By Fritz Haber . . . . .	325
Conservation of Natural Resources in Relation to Business. . . . .	By John J. Miller . . . . .	331
Sociological Work of the New Jersey Zinc Company. . . . .	By Florence Hughes . . . . .	333
Welfare and Safety Provisions at the Welsbach Company's Plants. . . . .	By Howard Lyon . . . . .	336
Cottonseed Flour as a Possible Food for Man. . . . .	By C. A. Wells . . . . .	338
WILLIAM H. NICHOLS MEDAL AWARD:		
Presentation Address. . . . .	By Bernhard C. Hesse . . . . .	339
The Existence of Free Radicals. . . . .	By M. Gomberg . . . . .	339
MORRIS LOEB MEMORIAL:		
Presentation Address. . . . .	By L. H. Baekeland . . . . .	343
Address of Acceptance. . . . .	By Charles F. McKenna . . . . .	345
OBITUARIES:		
Robert Kennedy Duncan . . . . .		346
George Westinghouse . . . . .		347
CURRENT INDUSTRIAL NEWS:		
Naphthalene as a Fuel for Motor Vehicles. . . . .		348
Removal of Blast Furnace Obstructions with Explosives . . . . .		349
Transportation of Chemicals by Water . . . . .		349
A New German Silk Mill . . . . .		349
Whale Oil . . . . .		349
Italian Auxiliary Marine Diesel Engine . . . . .		349
Local Surface Hardening of High Tension Steels. . . . .		349
The Spontaneous Combustion of Coal in Mines. . . . .		350
Some Statistics on German Universities. . . . .		350
Düsseldorf Centennial Exposition . . . . .		350
The Rubber Situation in Japan . . . . .		350
England's Chemical Trade 1912 and 1913 . . . . .		351
Electric Currents in Concrete . . . . .		351
Temperature Regulator . . . . .		352
Steam Raising by Gas Coke . . . . .		352
Engineering Report on Argentine Petroleum . . . . .		352
NOTES AND CORRESPONDENCE:		
The Use of Ozone in Ventilation. . . . .	By Ludwig von Kuppfer, of Berlin . . . . .	353
Operations of Steel Mills in March . . . . .		356
A Rapid Method for Casein in Milk—Correction. . . . .		356
American Alcohol Insoluble Test for Shellac—Note. . . . .		356
PERSONAL NOTES . . . . .		
356		
BOOK REVIEWS:		
Der Stärkezucker: Chemische und technologisch behandelt; Natronzellstoff; Coast Erosion and Protection . . . . .		358
NEW PUBLICATIONS . . . . .		
360		
RECENT INVENTIONS . . . . .		
361		
MARKET REPORT . . . . .		
361		



## EDITORIALS

### THE WILLIAM H. NICHOLS MEDAL

In the year 1901 the New York Section of the Society discussed the advisability of establishing a Research and Medal Fund, the income from which was to be used for the encouragement of chemical research. A committee reported that in its judgment the establishment of a Medal Fund was not desirable but recommended the establishment of a Research Fund. It was further proposed that from the proceeds of such a fund, the sum of \$50 should be awarded annually for the best paper incorporating the result of original research in Chemistry read before the Section. On mature deliberation the Section decided against a monetary reward and almost unanimously decreed the establishment of a Medal instead.

Dr. William H. Nichols, a charter member of the Society and former Treasurer of the New York Section, became interested in the movement and offered to provide funds for the endowment of such a Medal and its necessary design and dies. He made no restrictions as to the award of the medal, except that it be given for the encouragement of original research in Chemistry, leaving the conditions entirely to the Section. The Section, by unanimous vote, accepted the gift, formulated rules for the award of the medal, and called it the William H. Nichols Medal. That the medal has accomplished its purpose, the character of the work for which it has been awarded speaks fully.

The founder of the medal has been heard to say that he has been profoundly impressed with the highly original and valuable research work in Chemistry which is accomplished in a most unassuming and modest way by the teachers in our universities and colleges without hope of material recompense, and that he had given a great deal of thought as to what to suggest and advocate in recognition.

Article II of the Constitution of our Society states: "The object of the Society shall be the advancement of Chemistry and the promotion of Chemical Research." It is believed that valuable results are being accomplished in the advancement of Chemistry through the publication of our Journals. What have we done as a great Society to promote Chemical Research? Have we lived up to our opportunities?

The interest accruing from the Life Membership Fund not required to protect the rights of Life Members will be available for the support of Research. By a recent vote of the Directors of the Society financial assistance to aid in defraying the legitimate expenses of chemical research may be given if the subject of the work meets with their approval. This certainly is a step in the right direction, but the amount available will enable the Directors to meet but a small fraction of the deserving demands. Is there not some way in which the funds for the support of meritorious research may be greatly increased? It is only through larger resources that we can attain

the second great object of the foundation of our Society and become a factor in the support and advancement of Chemical Research.

T. J. PARKER

### THE COMMISSION ON INDUSTRIAL RELATIONS

A trip to include the principal cities of the country was begun in March by the members and investigators of the Federal Commission on Industrial Relations, which is to make an inquiry into irregularity of employment, the possibility of increasing production through scientific management, the activities of employers' associations and trade unions, and similar industrial problems of moment. It is announced that the Commission will especially endeavor to bring together manufacturers who are in the habit of shutting-down during certain periods of the year, in the hope that some way may be devised whereby employers may agree to close down at different times, thereby providing practically continuous employment for wage earners. In order that it may be enabled to properly perform its functions in collecting information, conducting investigations and determining facts, the Commission is properly invested with authority to secure all statements that it desires. Every interest is to be given a hearing, and, while witnesses may be summoned, voluntary testimony from persons looking to the general betterment of conditions is said to be welcome.

It is indeed difficult to frame specific business and industrial legislation without carrying the efforts of it to almost absurd lengths; but, while some prominent manufacturers predict that this investigation into industrial relations will effect little in the way of reform in the case of concerns which have learned their business lessons under severe competitive conditions, the results will be awaited with interest by those favoring a constructive course of procedure. However, the information obtained should be accessible to the public only upon approval of the Commission itself, in order that there may be some reasonable inquiry into the purpose of the applicant for the information. Publicity has accomplished more than even drastic legislation in industrial reform, but to make the material secured by the Commission available to all would not be demanded by the public welfare in this case.

This Commission might also assume the responsibility for effecting certain of the results sought in the Trade Relations Bill, some of the provisions of which aim at eliminating practices which should be condemned.

W. A. HAMOR

### TRADE IN CHEMICALS AND CHEMICAL PRODUCTS BETWEEN GERMANY AND THE UNITED STATES IN 1913

The statistics relative to the foreign trade of Germany during 1913, dealing with the export and import

TABLE I IN UNITS OF 100 KG. = SUBSTANTIALLY 0.1 LONG TON

Official German class	PRODUCT	U. S. exports to	U. S. imports from	BALANCE IN FAVOR OF	
		Germany	Germany	U. S.	Germany
I	Malt, oil fruits, plants, etc.	3,403	11,284		7,881
II	Industrial or medicinal vegetable products.	4,567	33,171		28,604
III	Tanning extracts.	3,213		3,213	
IV	Resins, gums and adhesives.	787,296	7,985	779,311	
V	Caoutchouc and camphor.	3,781	34,671		30,890
VI	Animal and vegetable fats and oils.	1,482,240	197,040	1,285,200	
VII	Animal products.	135	10,821		10,686
VIII	Starch and sugar.	11,050	158,298		147,248
IX	Alcohol, acetic acid, mineral waters.		20,419		20,419
X	Mineral and fossil raw materials.	4,317,449	696,514	3,620,935	
XI	Ores, iron and slags.	141,320	30,678	110,642	
XII	Fossil fuels.		192,156		192,156
XIII	Mineral oils and like fossil raw materials.	7,466,897	21,707	7,445,190	
XIV	Coal-tar oils and products.		221,748		221,748
XV	Waxes.		1,116		1,116
XVI	Soap and fat products.	79,307	13,033	66,274	
XVII	Chemical and pharmaceutical products.	326,378	12,327,989		12,001,611
XVIII	Miscellaneous chemical and pharmaceutical products.	809	40,825		40,016
XIX	Dyes and dye materials.	39,276	299,178		259,902
XX	Ethers and alcohols.	50,707	714	49,993	
XXI	Volatile oils, synthetic perfumes, toilet articles.	271,319	4,916	266,403	
XXII	Artificial fertilizers.		254,475		254,475
XXIII	Explosives and combustibles.	119	3,800		3,681
XXIV	Wood fiber and chemical paper.	7,893	354,220		346,327
XXV	Metals.	4,177,136	194,582	3,982,554	
TOTALS		19,174,295	15,131,340	17,609,715	13,566,760

of drugs, medicines, dyewares, and the various commodities related to chemical industry, have just become available (*Chemiker-Zeitung*, Feb. 3, 1914, pp. 169-76). From this source of information, the following tabulations have been compiled, showing the exchange of chemical products between the United States and Germany. The figures given are in units each of 100 kilograms, or one-tenth of the metric ton which is substantially the long ton of this country. No account has been taken of fractions, which are involved only in the precious metals, and the alkalis.

The tables show a total metric tonnage of 3,430,564, of which 1,917,430 metric tons represent exports from the United States to Germany, and 1,513,134 metric tons represent imports into the United States from Germany; that is, practically 56 per cent of the gross are exports to Germany, and 44 per cent of the gross are imports from Germany. Comparison with the information given in *THIS JOURNAL*, 6, 2, is not easily possible, since the values of the imports and exports involved in 1913 are not now known, and tonnage-figures for 1904 are not readily accessible.

Table I displays with respect to each of the twenty-five classes of merchandise, the tonnage movement originating in each country, and the excess for each class. Out of the 25 classes, Germany excels in 15 and the United States in 10.

Table II shows for each class the movement in each direction, under each of the sub-classes involved. There is a total of twenty-five different classes with a grand total of 229 sub-classes. In none of the sub-classes involving more than one specific merchandise, is it shown how the tonnage is distributed over individual articles. Nevertheless, these tables cannot be otherwise than suggestive and helpful.

TABLE II IN UNITS OF 100 KG. = SUBSTANTIALLY 0.1 LONG TON

Official German sub- class	U. S. exports to Germany	U. S. imports from Germany
I—MALT, OIL FRUITS, INDUSTRIAL PLANTS, FRUITS AND PLANT JUICES		
30 Hops.		11,119
32 Madder, quercitron and other dye plants.	3,403	
60a Opium.		165
II—INDUSTRIAL OR MEDICINAL VEGETABLE PRODUCTS		
72c Lichens, herbs, berries, leaves and buds.	4,567	5,499
73 Vegetable wax.		1
89 Sawdust and excelsior.		27,671
III—TANNING EXTRACTS		
384c Miscellaneous tanning extracts.	3,213	
IV—RESINS, LACQUER AND VARNISH GUMS, ADHESIVES		
97a Turpentine rosin.	770,100	2,619
97c Damar; hard and soft gums and resins.	11,168	560
97e Shellac.		1,179
97f Gum acacia, Bassora gum, etc.		1,027
97s Gum tragacanth.		625
342 Alcohol and shellac varnishes.	84	
343 Miscellaneous and coach varnishes.	4,447	1,975
345 Putty and miscellaneous putties.	829	
346 Asbestos paint and putties.	668	
V—CAOUTCHOUC AND CAMPHOR		
98a Caoutchouc, crude or refined.	364	20,019
98b Gutta percha, crude or refined.	272	911
98d Rubber scrap and waste.	3,145	13,741
VI—ANIMAL AND VEGETABLE FATS AND OILS		
126a Hog lard.		1,011,812
126b Oleomargarine.		196,328
126c Goosefat, beef-marrow, etc.		1,091
128b Prime beef tallow.		85,998
129 Beef and mutton tallow.		35,498
130 Bone-fat, fat-waste, stearin-tar.	16,809	37,005
131a Fish oils.		6,417
166d Peanut oil.		16,058
166h Cotton-seed oil.	99,950	
166l Beechnut, bone, corn, poppy, sunflower, etc., oils.	19,127	
168 Cocoa-butter.		4,798
170 Cotton-stearin.	3,335	
171b Palm oil.		136,684
171c Coconut oil.		2,150
172 Oleic acid, olein, etc.	5,875	
205b Edible vegetable fats.		345

TABLE II—IN UNITS OF 100 KG. = SUBSTANTIALLY 0.1 LONG TON (Continued)

Official German sub-class		U. S. exports to Germany	U. S. imports from Germany	Official German sub-class		U. S. exports to Germany	U. S. imports from Germany
VII—ANIMAL PRODUCTS				XVI—SOAP AND FAT PRODUCTS (Concluded)			
142	Spermaceti	135	..	258	Vaseline and lanolin	10,285	..
156f	Bones and hoofs	..	10,821	260	Lubricants made of fats or oils	68,384	..
VIII—STARCH AND SUGAR				262	Shoe polish	243	..
173a	Potato starch, wet, dry or ground	..	15,222	264	Stearin, paraffin materials	395	..
173c	Corn, wheat and other starches	5,833	..	XVII—CHEMICAL AND PHARMACEUTICAL PRODUCTS			
174	Starch-gums (dextrin), roasted starch and gluten	..	19,460	266	Alkali and other metals	..	411
176c	Beet sugar, all forms, refined	..	22,112	270	Sulfur and Spence metal	71,535	..
176f	Beet sugar, raw	..	101,504	276	Oxalic acid and potassium oxalate	..	26,066
177a	Glucose, etc.	5,217	..	277	Acetic anhydride	..	832
IX—ALCOHOL, ACETIC ACID, YEAST, MINERAL WATERS				278	Lactic acid and lactates	..	2,040
190	Mineral waters, inclusive of bottles	..	20,419	279a	Tartaric acid	..	1,235
X—MINERAL AND FOSSIL RAW MATERIALS				280c	Crude salts of 12-15 per cent $K_2O$	..	5,412,614
223a	Clay (potter's pipe, fire, etc.)	..	223,922	280d	Salts of more than 15-19.9 per cent $K_2O$	..	412,926
224d	Graphite, crude, ground and washed	10,763	..	280e	Fertilizer salts and fertilizers with 38 per cent $K_2O$	..	2,168,204
225a	Pumice and tripoli, crude, ground and washed	1,761	..	280f	"Abrum" and miscellaneous salts	..	131,626
225c	Mineral abrasives polishes and rouges	..	6,675	283	Barium chloride	..	13,434
227b	Magnesite	..	10,856	289b	Caustic potash, solution or solid	..	38,173
227d	Phosphate rock and other mineral phosphates	4,212,124	..	290	Potassium carbonate	..	78,339
230a	Portland, etc., cement	..	104,423	292	Bleaching powder, barium and hydrogen peroxide, etc.	..	82,634
231b	Asbestos, crude and in fibers	48,151	..	295a	Potassium sulfate	..	536,741
231c	Mica	575	442	295b	Potassium phosphate	..	13
232a	Heavy spar and celestite	..	350,196	298a	Alums, acetate of alumina, alumina, etc.	..	7,605
236a	Boronatocalcite, etc.	2,088	..	299	Chrome-iron and copper alums	..	4,794
236c	Miscellaneous earths, e. g., Fuller's earth, etc.	41,987	..	304b	Barium nitrate	..	6,078
XI—ORES, IRON AND SLAGS				306	Potassium manganate and permanganate	..	3,978
237a	Antimony ores and matte	..	210	308a	Potassium and sodium ferro- and ferricyanide	..	10,179
237f	Gold ores	..	4	308b	Potassium and sodium cyanide	..	25,619
237g	Copper ores and cuprous cinder	2,501	25,854	309a	Acetate of lime	203,643	..
237h	Manganese ores	..	4,610	311	Crude and refined argols	..	1,284
237o	Zinc ores	132,088	..	312	Tartar emetic and other antimony products	..	2,077
237q	Uranium, molybdenum and other miscellaneous ores	6,731	..	314	Strontium carbonate, oxide and chloride	..	903
XII—FOSSIL FUELS				315	Zinc chloride and other zinc salts	..	489
238d	Coke	..	185,492	316b	Carbides of aluminum, silicon, etc.	18,261	..
238h	Vegetable charcoal	..	6,664	317a	Sulfate of ammonia	..	56,296
XIII—MINERAL OILS AND OTHER FOSSIL RAW MATERIALS				317b	Arsenious acid	..	10,947
239a	Mineral lubricants	1,024,673	8,415	317c	Epsom salts	..	46,816
239b	Crude petroleum, etc.	1,619	..	317d	Chlorides of magnesium and calcium	..	68,771
239c	Heavy benzine, patent-turpentine	18,194	..	317e	Potassium chloride	..	2,611,137
239d	Gas oil	55,468	..	317f	Potassium magnesium sulfate	..	222,978
239e	Refined petroleum	5,747,587	..	317g	Lime-nitrogen, nitro-lime and other fertilizers	..	231,976
239f	Crude benzine	418,159	..	317h	Nitrites	..	4
239g	Benzine, ligroin and other miscellaneous light distillates	15,712	..	317n	Salicylic acid and salicylates; santonin; benzoic acid and benzoates	..	2,672
239h	Miscellaneous crude mineral oils	18,746	..	317o	Ammonium chloride	..	19,127
250b	Crude hard paraffin	87,028	..	317s	Sodium sulphydrate, lead compounds and miscellaneous metalloids, acids, salts	32,939	88,971
251	Soft paraffin	100	..	XVIII—MISCELLANEOUS CHEMICAL AND PHARMACEUTICAL PRODUCTS			
240a	Asphalt and asphaltic minerals	68,116	..	371	Scrap Welsbach mantles	..	32
241	Crude ozokerite, etc.	11,443	..	372	Dried or powdered egg albumen	..	1,308
249	Refined ozokerite, etc.	52	5,214	373	Casein and products for technical uses	..	1,658
243a	Pitch	..	8,078	375a	Glue exclusive of albumen	..	23,180
XIV—COAL-TAR OILS AND PRODUCTS				375b	Gelatin	..	4,839
245b	Anthracene and heavy oils	..	159,944	376	Gelatin capsules	1	540
246a	Naphthalene	..	7,242	378	Wood and peat tar creosote	..	180
246c	Phenol, crude or refined	..	12,098	380a	Quinine, salts and compounds	..	635
246d	Cresol	..	2,152	380b	Other alkaloids and their salts or compounds	3	444
246e	Anilin oil and salt	..	24,282	386	Artificial balsams and non-odoriferous watery extracts	389	240
246f	Naphthol and naphthylamin	..	6,379	388	Proprietary remedies	416	1,010
246g	Anthraquinone, nitrobenzol, toluidin, resorcin, phthalic acid and other like materials	..	9,651	390a	Miscellaneous medicinals	..	968
XV—WAXES				390b	Miscellaneous chemicals for photographic cleansing and other uses	..	5,521
247a	Beeswax	..	1,116	—	Miscellaneous pharmaceuticals and chemicals	..	280
XVI—SOAP AND FAT PRODUCTS				XIX—DYES AND DYE MATERIALS			
254	Soft and textile soaps; Turkey-red oil, etc.	..	6,208	318b	Animal kirmes, carmine, sepia	25	..
256	Soap in cakes, powder, liquid, etc.	..	481	319	Anilin and other coal-tar dyes	..	138,547
257a	Crude glycerin	..	5,037	320a	Alizarin-red	..	4,926
257b	Refined glycerin	..	1,307				



TABLE II.—IN UNITS OF 100 KG. = SUBSTANTIALLY 0.1 LONG TON (Concluded)

Official German sub- class	U. S. exports to Germany	U. S. imports from Germany	Official German sub- class	U. S. exports to Germany	U. S. imports from Germany
XIX—DYES AND DYE MATERIALS (Concluded)			XXIV—WOOD FIBER, CHEMICAL PAPER		
320b		21,636			
321a		34,609	650b	7,545	352,468
322		1,056			
324b	4,848		664	348	1,752
325		24,208			
326a	18,850	20,979			
326b		8,137			
326c		7,328			
327		306	769d	36	
328a	2,775		769e		
328b	1,225				
329c		18,716	772a	190	
330	9,537		772c	312	
331		6,616	777a		24,400
332b	1,226	8,530	777b		117,331
334	573				
336a		879	844	8,367	10,186
336b		295	850	162,727	
338	217		855a		17,697
340		2,210	860	9,285	10,412
XX—ETHERS AND ALCOHOLS			864	21,566	
348			869a	3,946,378	
		669	869b	5,111	1,977
349a	50,707		869c	23,162	5,931
351		45	869e		1,545
XXI—VOLATILE OILS, SYNTHETIC PERFUMES, TOILET ARTICLES			869f		5,094
352		65			
353a					
353c	269,945				
		1,374			
354					
358		1,842			
		298			
XXII—ARTIFICIAL FERTILIZERS					
359a		23,996			
360		82,838			
361		105,481			
362		42,160			
XXIII—EXPLOSIVES, AMMUNITION AND COMBUSTIBLES					
366	119	953			
370		2,847			

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## ORIGINAL PAPERS

THE RELATION OF COMPOSITION OF ASH IN COAL  
TO ITS FUSING TEMPERATURE<sup>1</sup>

By OSCAR W. PALMENBERG

One of the most troublesome features in the combustion of coal is that due to the production of clinker. The production of clinker influences the rate of combustion and the cost of maintenance especially where automatic stokers are in use. A coal may clinker so readily under certain conditions that it becomes unfit for use irrespective of its fuel value. It is, therefore, of the greatest importance to know whether a coal will clinker under the conditions for which it is required. When coal is burned under a boiler for the production of steam it is especially important to know whether the ash will clinker and at what temperature.

The production of clinker, as is well known, is due to the fact that the ash of the coal, which is the liberated mineral matter, is exposed to a temperature sufficient to fuse it, causing it to form a viscous mass which will

flow and form cakes and thereby clog up the spaces between the burning particles of coal or coke. The mass of fused material offers resistance to the flow of air and robs the coal of the necessary oxygen to support combustion. If the draft cannot be increased to overcome this resistance the rate of combustion is diminished, other things being equal, in proportion to the amount of clinker formed.

To determine whether a coal will clinker, that is, whether the coal has an ash which will fuse at a low temperature, has been undertaken in several ways and many have believed that an analysis of the ash, or the iron in the ash, or the sulfur in the coal will give the explanation.

To show that there is no relation between the clinkering quality of a coal and the sulfur or iron content, the writer has made this investigation. The following analyses of the ash together with the fusing temperature determinations on a wide range of coals will readily show that no conclusion can be obtained from a chemical analysis.

<sup>1</sup> Presented before the New York Section of the Society of Chemical Industry, The Chemists' Club, New York, November 21, 1913.

The ash of coal is composed mainly of silica ( $\text{SiO}_2$ ), iron oxide ( $\text{Fe}_2\text{O}_3$ ), aluminium oxide ( $\text{Al}_2\text{O}_3$ ), calcium oxide ( $\text{CaO}$ ), magnesium oxide ( $\text{MgO}$ ), sodium oxide ( $\text{Na}_2\text{O}$ ), potassium oxide ( $\text{K}_2\text{O}$ ), carbonates ( $\text{CO}_2$ ), sulfates ( $\text{SO}_3$ ) and small amounts of phosphates. Since all coals, but particularly soft coals, consist of a mixture of pure coal substance and pyrites, bone, slate, fire-clay, etc., these elements will be present in a variable proportion depending upon the nature of the coal vein and the method and care by which the coal is extracted from the ground. In making an analysis, therefore, of a coal sample representing a mixture of all these materials, a definite percentage of the component parts of the ash may be obtained but this analysis does not tell us how much pyrites, bone, slate, fire-clay, etc., is present. It is, therefore, apparently impossible to judge from this analysis whether the ash will have a high or low fusing temperature. It is true that the pyrites will fuse at a lower temperature than the slate, but since both may contain iron, the analysis does not indicate a method of arriving at a conclusion to show the fusibility of the ash due to the iron content. The problem offered is very similar to that when trying to determine a formula by which the heat value in a coal may be estimated. This has been tried by using the percentage of ash and volatile matter or ash and fixed carbon, but since these constituents are so variable in their composition, depending upon their sources, it is impossible to arrive at a reliable method. For this reason a calorimetric determination must be made.

The following analyses and fusing temperature determinations were made on coals, most of which were mined in Pennsylvania and samples were obtained either from the mine or place of consumption:

TABLE I—FUSING TEMPERATURES AND COMPOSITION OF THE ASH OF BITUMINOUS AND SEMI-BITUMINOUS COALS

No.	Fus. temp. of ash ° F.	$\text{SiO}_2$	$\text{Fe}_2\text{O}_3$	$\text{Al}_2\text{O}_3$	$\text{CaO}$	$\text{MgO}$	$\text{Na}_2\text{O}$	$\text{K}_2\text{O}$ $\text{SO}_3$	S in coal	Ash in coal
1.	2700	51.93	4.81	36.82	3.84	1.00	1.60	0.51	5	15
2	2615	44.74	14.14	36.91	2.18	0.41	4.85	1.46	7	88
3	2600	48.83	6.28	42.62	1.64	0.30	3.90	1.01	9	15
4	2600	54.18	7.29	34.53	3.01	0.47	0.52	0.90	6	41
5	2400	40.61	22.26	32.94	1.77	0.51	1.91	2.06	9	70
6	2372	30.67	39.88	25.31	2.63	0.39	1.71	2.41	8	96
7	2309	47.94	17.95	28.47	4.17	0.51	0.96	2.11	11	04
8	2300	46.40	13.84	35.30	3.58	0.31	0.57	1.80	13	51
9	2300	30.90	35.13	31.14	2.00	0.52	0.31	1.13	6	25
10	2246	35.48	30.67	30.73	2.10	0.44	0.28	2.17	7	90
11	2180	29.37	38.75	29.52	1.57	0.37	0.44	3.97	10	60

## COMPARISONS

No.	Fus. temp. of ash	No.	Fus. temp. of ash	Iron oxide
2.	14.14 2615	7.	2309	17.95
8.	13.84 2300	8.	2300	13.84
		9.	2300	35.13
6.	39.88 2372	5.	2400	22.26
11.	38.75 2180	6.	2372	39.88

It may be noted from these tables that some coals have ash of like iron content and variable fusing temperature, then again others have ash of like fusing temperature and variable iron content.

It would appear from these analyses that there is no relation between the percentages of the various

constituents of the ash and the fusing temperature. Therefore, a chemical analysis is of no value to arrive at a conclusion regarding the clinkering quality of a coal. It may be noted that although coals having an ash with a very low iron content seem to give the highest fusing ash, no definite fusing temperature

TABLE II—FUSING TEMPERATURES OF ASH IN COALS ARRANGED ACCORDING TO THE IRON CONTENT

No.	Iron oxide	S in coal	Ash Fus. temp. ° F.	No.	Iron oxide	S in coal	Ash Fus. temp. ° F.
1.	3.34	0.69	10.77 2950	33.	15.21	1.42	7.98 2400
2	4.8	0.64	7.19 2730	34.	15.38	1.57	2156
3.	4.35	0.58	5.81 2850	35	15.53	...	2291
4	4.81	0.51	5.15 2700	36.	15.89	1.22	9.74 2610
5.	5.91	0.73	2912	37.	16.00	1.63	9.90 2309
6	6.28	1.01	9.15 2600	38.	17.95	2.11	11.04 2309
7.	7.29	0.90	6.41 2600	39.	19.19	1.79	7.90 2138
8.	7.34	...	15.57 2850	40.	19.54	2.41	11.33 2380
9.	7.44	...	2408	41	22.38	4.56	2210
10.	7.62	...	2900	42	22.55	2.09	2516
11.	7.88	0.74	5.57 2600	43.	22.57	2.00	9.03 2336
12.	7.94	1.52	15.61 2750	44.	22.86	...	7.23 2372
13.	8.78	1.04	7.46 2642	45.	23.17	1.16	9.52 2535
14.	9.19	...	2600	46.	23.30	2.40	8.10 2156
15.	9.23	1.59	19.63 2822	47.	24.40	2.23	10.90 2190
16	9.62	0.89	11.36 2950	48.	26.50	2.13	6.86 2192
17	10.13	1.59	17.64 2768	49.	27.22	3.13	13.54 2138
18.	10.40	1.09	2678	50.	28.39	1.96	6.65 2084
19.	10.69	...	2660	51.	28.81	2.32	7.55 2318
20.	10.97	...	2252	52.	30.42	3.14	10.32 2246
21.	11.19	0.97	2732	53.	30.67	2.17	7.90 2246
22.	11.24	...	2372	54.	33.27	2.86	9.33 2520
23.	11.28	1.04	8.53 2745	55.	35.13	2.13	6.25 2300
24.	11.40	0.63	2516	56.	36.12	3.04	8.40 2264
25.	12.27	1.04	8.32 2830	57.	36.17	2.60	7.50 2500
26.	12.77	1.01	9.02 2678	58.	38.12	...	2300
27.	13.47	...	2534	59.	38.62	3.26	10.11 2100
28	13.82	1.36	2543	60.	38.75	3.97	10.60 2180
29.	13.84	1.80	13.51 2300	61.	39.51	2.97	8.22 2210
30.	14.14	1.46	7.88 2615	62.	39.88	2.41	8.96 2372
31.	14.54	1.32	14.83 2210	63.	40.93	2.68	9.08 2415
32.	15.15	1.07	6.38 2560	64.	44.39	3.51	9.34 2318

fits a definite percentage and when the iron content goes beyond 10 per cent the fusing temperature cannot be judged at all. That the sulfur content of the coal has no bearing whatsoever upon the fusibility of the ash is also apparent.

The writer intends to continue this investigation on coals from other sources with the object of determining whether there may not be some having practically no iron and showing a low fusing ash.

Since the sulfur occurs in coal combined either with iron, lime or the hydrocarbons there naturally exist innumerable combinations and for this reason the sulfur content cannot be used as an index to clinkering. Only in those cases in which the sulfur is in combination with the iron in the form of pyrites would it be possible to judge the clinkering property, if the iron content in the ash had any bearing upon the fusing temperature.

The fusing temperature determination of the ash in coal will, in the future, displace the sulfur determination in such coals used for steaming purposes and will readily show the fallacy of buying and selling coal on an analysis basis where specifications are used containing sulfur tables penalizing beyond a certain guaranteed amount of sulfur.

It has been quite a common practice to place 1.50 per cent sulfur as a limit and penalize as much as four

cents per ton for every 0.25 per cent above 1.50 per cent. The injustice of this practice is very evident as it often happens that coals with a high sulfur content are extremely high in heat value and do not clinker readily at all. Since the sulfur has no appreciable effect upon the metallic parts of the furnace, it need therefore not be considered in the selection of a coal for steaming purposes.

To arrive at the value of a coal for steaming purposes it is therefore just as essential to make the fusing temperature test of the ash as it is to make the calorimetric determination. If these determinations are made an explanation is readily had as to why two coals of apparently like proximate analyses will give entirely different evaporations when fired under like conditions.

50 EAST 41ST STREET, NEW YORK

### "FREE CARBON"

#### Its Nature and Determination in Tar Products

By JOHN MORRIS WEISS

Received January 26, 1914

All tars contain a substance in greater or lesser amount, which has been called "free carbon." This has usually been considered as the material insoluble in hot benzol, and is not pure elemental carbon, but a mixture of this substance with insoluble hydrocarbons and other compounds of high carbon content. The amount of this free carbon varies quite considerably in tars from various sources, depending on the original coal and also, to a large extent, on the temperature of carbonization and the degree of superheating to which the developing tar vapors were subjected. Under like conditions, the higher the temperature the greater the amount of free carbon found in the tar produced. The extent to which free carbon varies in tars from various sources may be shown in the following typical analyses of a number of tars:

KINDS OF TAR	Percentage free carbon by toluol-benzol method
Semet-Solvay coke oven.....	10.76
Koppers coke oven.....	6.79
United Otto coke oven.....	13.38
Horizontal retort gas works.....	37.47
Horizontal retort gas works.....	28.91
Inclined retort gas works.....	24.31
Vertical retort gas works.....	3.95
Water gas.....	0.02
Water gas.....	0.38
Oil gas tar.....	1.18
Blast furnace.....	15.89
Lignite.....	1.79
Hardwood.....	0.02
Pine.....	0.03

All these analyses were taken on the dried tars, that is, the samples of tar were distilled until all water was removed, any oil distilling with the water being separated and returned to the distilling vessel after the water was completely driven over.

As stated before, this insoluble material is not pure carbon. One analysis by Donath and Asriel<sup>1</sup> showed

Hydrogen.....	2.3
Nitrogen.....	3.7
Oxygen.....	7.13
Carbon.....	89.3

This analysis adds up to over 100, but the writer can

<sup>1</sup> Lunge's "Coal Tar and Ammonia," 4th ed., p. 241.

give only the figures as found by him in the reference. Hubbard and Reeve<sup>1</sup> have made several ultimate analyses of so-called free carbon, with the following results:

	From	To
Carbon.....	90.17	94.26
Hydrogen.....	2.50	3.31
Oxygen.....	1.81	3.91
Sulfur.....	0.50	1.78
Nitrogen.....	No trace upon a qualitative test.	

They also made analyses of sulfur on various precipitates obtained by digestion of tars with carbon bisulfide for various periods, the results seeming to indicate a combination of tar with the solvent.

One analysis of average free carbon from coal tars made in the writer's laboratory showed

Carbon.....	89.85
Hydrogen.....	3.30
Nitrogen.....	1.10
Oxygen.....	3.13 (by difference)
Sulfur.....	1.28
Mineral ash.....	1.34

The free carbon used for this analysis was obtained by the toluol-benzol method, which is described in detail in a later part of this paper.

Many methods have been proposed for the estimation of free carbon. Kraemer<sup>2</sup> extracts the tar with forty times its volume of xylol. Köhler<sup>3</sup> heats 10 grams of tar with 25 grams of glacial acetic acid and 25 grams of toluol, pours the mixture on two filters of equal weight placed inside of each other, and washes with hot toluol until colorless. Kraemer and Spilker<sup>4</sup> mix the tar with twenty parts of xylol, filter off the insoluble material, wash with five parts of xylol, and dry on the filter. The same authors give another method which consists of mixing one part of tar with three parts of aniline, pouring the liquid mass on a porcelain plate of special shape. The insoluble carbon remains as a heavy mass after the liquid has been sucked into the porcelain and is removed with a wooden spatula, dried and weighed. The statement is made that this method gives from 2-3 per cent lower results than the xylol method described, due to the greater solubility of the tar bitumens in aniline. Hodurek<sup>5</sup> has found that some solvents, of which benzol, acetic acid and ether are mentioned, have a precipitating action on bituminous substances, such as those contained in coal tar, and has devised a method based on filtration of the original undiluted tar to determine the real free carbon. The method is, however, cumbersome and not adapted for practical work.

Hubbard and Reeve,<sup>6</sup> after a comparison of various methods, proposed the use of cold carbon bisulfide as the solvent in testing tars for free carbon. The method was claimed to be equally applicable to both tar and asphalt products. These authors also make mention of the progressive formation of further insoluble matter when the filtrates are allowed to stand,

<sup>1</sup> Proc. Am. Soc. Testing Materials, **11** (1911), 665.

<sup>2</sup> Lunge's "Coal Tar and Ammonia," 4th ed., p. 426.

<sup>3</sup> Z. angew. Chem. (1888), 677.

<sup>4</sup> Muspratt's Indus. Chem., **8** (1900), 3.

<sup>5</sup> Oesterr. Chem. Zeit. (1904), 365.

<sup>6</sup> Proc. Am. Soc. Testing Materials, **10** (1910), 420.



and ascribe this phenomenon either to sedimentation or to a combination of tar and solvent. S. R. Church, in discussing this paper, objects to the use of this method for testing tar products, contending that for these materials the use of two solvents is desirable, and that a hot extraction is necessary. The method suggested by him and later published in connection with other methods for testing tars, oils and pitches,<sup>1</sup> involves the use of toluol and benzol, and will be fully described in a later portion of this paper. Later, Church<sup>2</sup> described an improved form of extraction apparatus, a modification of one proposed for other uses by H. J. Cary-Curr.<sup>3</sup>

Recently, in a book published by Arthur R. Warnes,<sup>4</sup> there is described a method devised by Hooper and a modification of same by Warnes. This method involves the use of cresylic acid and 90 per cent benzol, and the writer has had no experience in its use, but objects to 90 per cent benzol and cresylic acid as solvents, because they are not definite chemical compounds which can always be obtained pure.

The remainder of this paper may be roughly subdivided into three parts. The *first* concerns work on the formation of insoluble compounds in mixtures of tar products and various solvents. The *second* comprises a comparison of various methods for "free carbon" or insoluble material determination, the work involved being carried out on a number of materials, both of pitch and asphaltic origin. The *third* portion involves a detailed description of the toluol-benzol "free carbon" method as developed in our laboratories, for tar and tar products, and decided after considerable experience and experimentation as the most convenient.

#### I—INSOLUBLE COMPOUNDS FORMED IN MIXTURES OF TAR PRODUCTS AND VARIOUS SOLVENTS

The experiments which are set forth in the first part of this communication were originally undertaken for the purpose of obtaining a tar free from insoluble residue, without otherwise changing the chemical constitution of the tar. As will be seen later, the attempts to this end were unsuccessful, but the results were very interesting, and led to the further experiments outlined below.

To remove free carbon, chloroform was first used as a solvent, because its low boiling point renders it easy to remove without superheating. Moreover, it has an odor distinct from that of the aromatic hydrocarbons, and its removal could be more or less accurately indicated by the odor of the residues handled. The tar selected was a coke oven tar, containing about 5 per cent of insoluble matter when tested by the toluol-benzol method. A weighed quantity of tar (about 500 grams) was diluted with about ten times its volume of pure chloroform and filtered twice through weighed thimbles made of a double thickness of S. and S. No. 575 hardened filter paper. When all material had been passed through the thimbles, these

were placed in the extractors and exhausted with hot chloroform. The extracts were refiltered through fresh thimbles, and again extracted. All the thimbles were dried at 100° C. and weighed. The combined filtrates and washings were brought into a tared flask connected to a condenser, and the bulk of the chloroform taken off on a steam bath. The condenser was then disconnected and the material was held at a temperature of 80° C. until it had regained its original weight, less the amount of insoluble matter removed. This latter amounted to 5.54 per cent. At this point, all odor of chloroform had completely disappeared.

This supposedly carbon-free tar was then tested by the toluol-benzol method, and also by a chloroform extraction to determine the percentage of insoluble matter. The results were:

	Original tar	Treated tar
Percentage insoluble in		
Toluol and benzol.	5.54	10.05
Chloroform.....	5.46	0.88

The inference to be drawn is obvious. On standing, chloroform formed a compound with the tar which is insoluble in benzol. This insoluble material is quite different in appearance from ordinary free carbon. The latter is dull black, and infusible, while this substance had considerable luster and could be sintered together by careful heating. Under the microscope it appeared slightly crystalline. No quantitative test was made on this substance, but on oxidation with fuming nitric acid, a very strong qualitative test was obtained in the resulting solution.

Following this, a similar amount of the same tar was treated in like manner, using pure benzol (benzene) as the solvent instead of chloroform. The tests of this treated tar were:

Percentage insoluble in	
Toluol and benzol.....	4.71
Benzol alone.	4.67
Chloroform..	2.17

This residue also did not resemble ordinary free carbon, being brown instead of black. Under the microscope, it appeared absolutely amorphous. On heating, it melted with decomposition and coking.

Slides were made of the original and treated tars, and viewed in a very thin layer with the microscope by transmitted light. Similar slides were also made, mixing a drop of one of the tars with a drop of the solvent. The magnification used was eighty-seven diameters. This examination confirmed the analytical tests, and threw further light on the subject. The results are given in the following table. The body of the slides appeared a clear, reddish brown, with the variations as noted in the following table.

The apparent meaning of the following results is that in the treated tars there is no real insoluble material of the same nature as ordinary free carbon, but that apparently materials have been formed which, though soluble in the complex mixture known as tar, yet are precipitated upon the addition of a solvent. These results indicate that both chloroform and benzol in contact with tar undoubtedly form compounds with some of the tar constituents, which compounds are at

<sup>1</sup> This Journal, 3 (1911), 227.

<sup>2</sup> *Ibid.*, 5 (1913), 195.

<sup>3</sup> *Ibid.*, 4 (1912), 535 and 856.

<sup>4</sup> Warnes', "Coal Tar Distillation," p. 146.

SLIDE NO.	MATERIAL	APPEARANCE
1	Original tar	Very granular with amorphous grains of various sizes.
2	Tar treated with chloroform	Clear, without grains.
3	Tar treated with benzol	Clear, without grains.
4	Mixture of No. 1 and benzol	Strongly granular.
5	Mixture of No. 1 and chloroform	Strongly granular.
6	Mixture of No. 2 and benzol	Very strongly granular.
7	Mixture of No. 2 and chloroform	Nearly clear.
8	Mixture of No. 3 and benzol	Granular and slightly crystalline.
9	Mixture of No. 3 and chloroform	Granular and fine, needle-like crystals.

least partly insoluble in benzol, and to a lesser degree, in chloroform. These three tars were also tested for fixed carbon and ash.

	Percentages fixed carbon	Ash
Original tar	15.42	0.13
Chloroform treated tar	14.65	0.02
Benzol treated tar	13.78	0.01

These results are also indicative, as the fixed carbon was not lowered as much as would be expected from the removal of over 5 per cent of material nearly all carbon. It would tend to show that simultaneously, higher, more complex bodies were formed which, on heating, give an increased coke residue. Possibly the chloroform may also form bodies of a trialkylmethane series, which would have this tendency to a very marked degree. It was not thought worth while to subject these residues to an ultimate quantitative organic analysis, as with an evident mixture of compounds, such results would show but little.

In the light of the foregoing results, experiments were then instituted to see whether, in the laboratory determination of free carbon, the results obtained would increase with the time the solvent and tar were allowed to remain in contact in the cold. The same tar was used for this work as in the previous experiments. Except for the time of standing with the first amount of solvent added, the general procedure in all cases was identical. In one series of tests, toluol was used as the digesting solvent; in another, benzol. In both cases benzol was used afterward in the extractor.

Time of standing	Percentage insoluble in benzol	Insoluble in toluol and benzol
0.25 hour	6.42	5.54
24 hours	6.65	6.30
90 hours	7.74	7.55
138 hours	9.25	8.44
258 hours	10.72	9.34

The longer the tar stands, the greater the amount of insoluble residue obtained. The reaction is evidently accelerated by the presence of a large excess of the solvent, and occurs equally with benzol and toluol. With only small amounts of benzol present, such as in an ordinary tar, it is conceivable that this reaction might take place with a very small velocity. In other words, with long time the amount of apparent insoluble matter in a tar might increase.

Experiments were then instituted by the writer to see whether carbon bisulfide and chloroform would give similar results. Tests similar to those with

benzol and toluol were made, using carbon bisulfide and chloroform separately, the material under trial being used both in the digestion and in the extractor. The following results were obtained on the same tar that was previously used:

Time of standing	Percentage insoluble in chloroform	Insoluble in carbon bisulfide
0.25 hour	5.91	5.84
48 hours	6.93	6.62
120 hours	8.27	7.37
216 hours	8.01	7.67
258 hours	8.21	7.52

A similar increase in apparent insoluble matter was noted here as with benzol and toluol, though not to the same extent.

The residues from the chloroform extraction were tested qualitatively for chlorine with positive results, but as no tube furnace was available, quantitative results could not be obtained. On the other hand, the residues from the carbon bisulfide extractions were assayed for sulfur by the "Eschka" method, the following figures being obtained:

Residue from a	Time of standing	Percentage sulfur
Benzol extraction	0.25 hr.	0.92
Carbon bisulfide extraction	0.25 hr.	1.46
Carbon bisulfide extraction	120 hrs.	1.82
Carbon bisulfide extraction	216 hrs.	1.67

This is conclusive proof that the solvents actually enter into combination with the tar constituents. The results can be explained on no other basis.

At various times, the writer has noticed in some of the German publications on tar products, that aniline, pyridine and glacial acetic acid have been suggested as the digestive solvent for free carbon determination. The following results were obtained using the material mentioned for digestion, and then in all cases after filtration, using benzol in the extractor:

Time of standing	Percentage free carbon by digestion with Aniline and benzol	Pyridine and benzol	Glacial acetic acid and benzol
0.25 hour	5.00	5.11	6.80
48 hours	4.81	5.23	7.01
144 hours	4.62	5.27	8.10

Here quite different results were obtained in the case of the first two solvents, aniline and pyridine. Acetic acid gives high results, and shows the phenomenon of progressive formation of insoluble compounds. It was also noted that, owing to its hygroscopic nature, water is easily absorbed and in this event, precipitates are formed which dissolve very slowly in the extractor. The pyridine is a very disagreeable substance with which to work, and is expensive and difficult to obtain in the pure state. The filtration of the aniline solution is a very slow and tedious operation, from four to five hours being required in many cases to pass 50 cc. through the thimble. In spite of the theoretical aspects of the matter, neither pyridine nor aniline seem to the writer to be suitable materials for a laboratory assay of free carbon.

It was then deemed advisable to try further experiments on various tar products. So far, but one tar had been used, and it was possible that this was a

peculiar material, giving rise to phenomena not shown by other similar substances. A series of experiments on various materials was made, comparing aniline and toluol as the digesting solvents, and using benzol afterward in the extractor.

	Aniline		Toluol	
	0.25 hour	72 hours	0.25 hour	72 hours
Coal tar No. 1.....	3.22	3.71	5.09	5.31
Coal tar No. 2.....	13.48	12.83	14.28	17.89
Coal tar pitch.....	8.68	9.08	13.22	15.13
Water gas tar.....	0.02	0.17	0.02	0.19

Besides, several substances were tested at 0.25 hour only, using aniline *versus* toluol:

	Aniline	Toluol
Water gas tar pitch.....	4.11	5.28
Coal tar roofing pitch.....	20.51	25.57
Coal tar briquette pitch.....	17.30	21.13
Coal tar paving pitch.....	13.08	16.72
Road compound.....	11.88	13.95

Various filtrates from this last set of tests were examined under the microscope by the hanging drop method. With both aniline and toluol, the first few drops filtered showed a very faint trace of insoluble matter; the remainder of the filtrate was in both cases perfectly clear when examined immediately. The aniline filtrate remained so, even after twenty-four hours' standing, but the toluol filtrates showed a gradual formation of insoluble matter in the form of amorphous grains. The formation of this precipitate was accelerated by further dilution with either toluol or benzol. The aniline solutions, similarly diluted, also showed precipitation, but of a quite different nature, being in the form of clear, fine, crystalline needles. The toluol filtrates showed precipitation on standing alone, the aniline filtrates only after the addition of benzol.

These results are of the same general nature as those with the first tar investigated. In water gas tar products, where the insoluble residue is very small, the differences between toluol and aniline are not marked. Tar No. 1, which shows no increase on standing with toluol, was unusually high in tar acids, and this factor may be the cause of its variable behavior. With substances varying as much as tars do, it would be too much to expect that all varieties would behave in exactly the same way, and it seems sufficient that a majority of those investigated showed similar phenomena when mixed with various solvents. For a practical laboratory test, neither aniline nor pyridine seem suitable. The latter, as before mentioned, is very disagreeable in its properties, expensive, and difficult to obtain pure. The difficulty of filtration of the aniline solutions is, to the writer's mind, sufficient in itself to exclude it from consideration for such purposes. Such difficulty is not encountered with toluol, carbon bisulfide, chloroform, etc. For a working method it would seem imperative to consider solvents of the general nature of these materials.

## II—COMPARISON OF VARIOUS MORE OR LESS WIDELY USED METHODS FOR DETERMINATION OF INSOLUBLE MATTER

### A. Cold carbon bisulfide method, using a Gooch

crucible-standard procedure of the American Society for Testing Materials.<sup>1</sup>

B. Toluol-benzol hot extraction method, using a cup made of filter paper.

C. Standard A. S. T. M. method, using cold carbon tetrachloride as the solvent.

D. The method used in C was supplemented by a hot extraction with the same solvent.

Besides these tests, another set was carried out, using carbon tetrachloride and cups of filter paper, and running exactly as in the toluol-benzol method. These results are not recorded because the experience was that results obtained by this procedure are not reliable, especially with tar products. After extraction and drying, the thimbles become very brittle and cannot, in many cases, be handled without loss. In some cases, also, with substances low in insoluble matter, an appreciable gain in weight was noted. The hot solvent and bitumen seem to form some compound which attacks the filter paper and causes disintegration. This is probably hydrochloric acid or chlorine compounds of some sort. An acid reaction was noted in the extraction flasks and in the recovery of carbon tetrachloride; the residues in the distillation vessel had a very strong smell of hydrochloric acid. This phenomenon was not exhaustively investigated, so that no positive assertion as to the cause can be made.

In these experiments, eighteen materials, comprising the most common types of pitches and asphalts, were selected and tested by the four methods mentioned above. All tests were made in duplicate, making 144 single determinations. The work was carried out by a single operator, and great care was taken to have as nearly as possible identical conditions in all cases. The solvents used were chemically pure, of the best obtainable grade. Thoroughly average samples of the various bitumens used were taken for the single determinations. In other words, every precaution was taken to eliminate all variations except those inherent in the particular method employed.

The results are given in the following table, two figures being given under each method, and representing the check determinations. The general consistency of the various materials was about 40° Dow taken at 77° F. for five seconds, under a load of 100 grams.

It was necessary in these tests to alter slightly the cold carbon bisulfide method when tar products were being handled. The slow solution of the last portion of these bitumens made complete washing a long and tedious affair. Accordingly, after the bitumen had been entirely brought into the crucible, the washing was carried on until about 150 cc. of carbon bisulfide had been used. The crucible was then allowed to stand over night in a stoppered bottle containing carbon bisulfide to a depth of about half the height of the crucible. Following this digestion, the washing could be completed with the use of 50–100 cc. additional carbon bisulfide. Precisely the same procedure

<sup>1</sup> Proc. Am. Soc. Testing Materials, 11 (1911), 245



	A S T M. method cold CS <sub>2</sub>		Benzol-tol. hot extr		CCl <sub>4</sub> cold Gooch		CCl <sub>4</sub> hot Gooch	
	1	2	1	2	1	2	1	2
Coal tar pitch, horizontal gas retort.....	34.76	35 05	34.50	35.30	42.41	42.26	38.77	37.94
Coal tar pitch, inclined gas retort.....	32 07	31 95	30.99	30.67	38.22	38.95	34.78	34.85
Coal tar pitch, vertical gas retort.....	10.16	10 47	7 80	8 09	17.25	17 50	15 38	15.90
Coal tar pitch, coke oven.....	19.83	19 64	20 92	21.31	30.38	31.75	27 24	27.01
Coal tar pitch, coke oven.....	17.26	17 47	18.40	18.26	25.97	26.50	23.09	23.41
Water gas tar pitch.....	2.02	1 98	4.73	5.19	10.31	10.76	9.02	9.21
Water gas tar pitch.....	1.60	1 46	7.92	7.71	14.83	13.31	11.93	11.77
Blast furnace tar pitch.....	30.20	29 70	28.76	27.95	34.87	35.32	32.82	32.31
Pine tar pitch.....	4.68	4 60	8.00	7.59	11.67	11.47	11.41	10.97
Stearine pitch.....	4.61	4 70	(a)					
Bermudez asphalt.....	5.49	5 43	5.53	5.70	5.73	5.78	5.61	5.71
Trinidad asphalt.....	24.38	24 43	22.21	22 86	23.34	23.89	22.30	21.17
Gilsonite fluxed.....	0.14	0 37	0.04	0.07	0.23	0 29	0 24	0.26
Grahamite fluxed.....	0.12	0 12	0 0	0 0	0.37	0.32	0.30	0.32
California asphalt.....	0.46	0 45	0.27	0.39	0.43	0.41	0.43	0.41
Mexican asphalt.....	0 30	0 29	0.57	0 47	0.30	0.40	0.30	0.40
Texas blown asphalt.....	1 11	1 33	1.26	1 36	1.13	1.09	0.96	0.96
Texas straight run asphalt.....	1.25	1 36	1.71	1 84	1.83	1.51	1.85	1.48

(a) Not considered worth recording.

was necessary when carrying on the cold carbon tetrachloride tests.

Comparing the figures obtained by the hot toluol-benzol method with those of the cold carbon bisulfide method, it will be seen that for the coal tar products in general, approximately the same results are obtained. The one exception is the vertical retort tar pitch, which is notably higher by the cold carbon bisulfide test. The water gas tar pitches give markedly higher results when tested by hot toluol and benzol, a phenomenon which must be explained by the nature of these bitumens, which are quite different from coal tar products. The pine tar pitch is also lower by the carbon bisulfide test in somewhat lesser ratio than the water gas tar products, but nevertheless, striking. All the asphalt products show approximately the same results by both methods, except the Trinidad asphalt, which gives slightly lower figures by the hot extraction with toluol and benzol.

Mention may also be made here of stearine pitch and its behavior in these tests. It dissolves with great difficulty in all of the solvents used, forming gummy masses which were very difficult to filter, and which were broken up only by long washing. The final residue was not "free carbon" in the ordinary sense of the word, but was a somewhat elastic, bituminous mass, which could be melted with decomposition at an elevated temperature. The results with benzol and with carbon tetrachloride on this material were so unsatisfactory and showed such poor concordance that they were omitted as worthless.

The cold carbon tetrachloride test, in all cases on tar products, gave much higher figures than those obtained with the other solvents used. The hot extraction gave lower results than with the cold solvent, but in no case as low as the results with carbon bisulfide or toluol-benzol. On the asphalts there is very little difference between the hot and cold solvent, and only minor variations between this material and the other solvents employed.

The carbon tetrachloride methods have never been considered as basic methods for an insoluble matter determination, but merely as a supplementary procedure to determine something of the nature of the bitumens soluble in other solvents. Therefore, it

would not seem necessary to consider it as a possible solvent for regular "free carbon" tests of tars and pitches. The writer will, therefore, confine himself to a consideration of the relative merits of the cold carbon bisulfide test and the toluol-benzol hot extraction.

On asphalts in general, the Gooch method using carbon bisulfide can be completed in a considerably less time than the toluol-benzol hot extraction, and the results obtained are equally as accurate. For this class of bitumens alone, it seems to be considerably more convenient. But it must not be forgotten that the toluol-benzol method can be used with accuracy on asphalts, and even though it consumes a longer total time, yet the actual time required for the operator is no greater. The extractor, once started, needs no especial attention. The carbon bisulfide cold method is, however, not readily applicable to tar products. It is troublesome and slow. All our experience tends to show that a cold solvent is not desirable for tars and pitches. For these materials, the hot toluol-benzol method is far more convenient and easy of application, and the writer has no hesitancy in recommending it. An aromatic solvent is the natural solvent for tar products, made up as they are of mainly aromatic compounds. Toluol and benzol are aromatic solvents, in fact, the only ones of this series low enough boiling to be applicable to this purpose.

### III—"FREE CARBON" METHOD RECOMMENDED

The writer would now turn his attention to a detailed description of the "free carbon" method recommended, using toluol and benzol as solvents. This method in all its essential details has been in use in all of the laboratories of the Barrett Manufacturing Company for a period of years, and has been adopted by a number of outside laboratories. So far as accuracy of results and ease of manipulation is concerned, it has, to the best of my knowledge, given satisfactory results. When the method was first proposed in essentially its present form, check tests on standard samples were made by six of our principal laboratories.

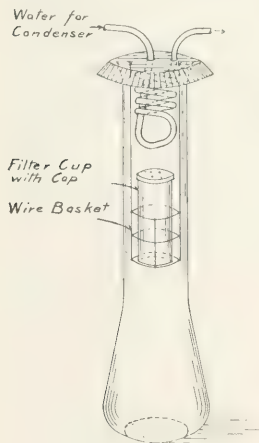
These results seem particularly good when one considers that these tests were undertaken when the method was first introduced, at which time the opera-

Percentages of free carbon in	Coal tar pitch No. 1	Coal tar pitch No. 2	Coal tar No. 1	Coal tar No. 2
Laboratory 1.....	23.40	38.13	28.67	12.24
Laboratory 2.....	24.26	36.44	28.61	13.31
Laboratory 3.....	23.40	39.40	28.80	13.30
Laboratory 4.....	23.41	40.79	29.52	15.26
Laboratory 5.....	24.03	40.71	29.27	13.48
Laboratory 6.....	23.70	38.43	29.49	13.19

tors in the various laboratories were not yet expert in the manipulation of the method. At present, much closer checks could be obtained, and such discrepancies as Tar No. 2, Laboratory 4, would be entirely obviated. Since this time (about five years ago) the principal changes have been in the form of the extractor, the steam bath, and supplementary apparatus. Following the results given in the early part of this paper, the operator should be cautioned against allowing the pitch or tar to digest too long with the toluol. At the outside, thirty minutes should suffice. This feature may have caused some of the discrepancies in check testing on the high side, as at the time of first putting forward this test, the possibility of formation of insoluble compounds was not recognized. All details of the test as standardized today, together with full descriptions of all apparatus used, are included in the following paragraphs.

#### APPARATUS

The extractor is shown in Fig. I, and is patterned after one described by H. J. Cary-Curr.<sup>1</sup> The principal



EXTRACTOR FOR  
FREE CARBON

FIG. I

requires but little ingenuity on the part of the operator.

Any type of steam or hot water bath will suffice for heating. We have, however, constructed in our own shops a bath for this purpose, which is very satisfactory in operation and, being compact, takes up very little space. It is constructed of copper and consists of a rectangular box eighteen inches long by five inches high. The width varies, depending on the number of extractors to be provided for. For an eight-extractor bath, a width of ten inches would be

<sup>1</sup> THIS JOURNAL, 4 (1912), 535 and 856.

used. Half way up from the bottom of the box is a perforated false bottom, on which the extraction flasks rest. Below this false bottom is a steam coil, entering and leaving through the side of the box. This coil is made of  $\frac{3}{4}$  inch copper pipe, strong enough to withstand the local steam pressure. An S bend through the box, giving about 54 inches of pipe, is ample. The top of the box contains two rows of four circular holes each, the openings having a diameter of two and seven-eighths inches. At each corner of the box are uprights carrying a plate of copper the same size as the top of the box, and six inches above it. This plate is cut out with openings directly over those on the top of the box and of the same size, this arrangement serving to steady the flasks. Four condensers are used in series, so that at one end of the box there is provided a water inlet with cock for each row of flasks. The box is filled with water, and the coil keeps this water hot enough to boil the benzol in the extraction flasks. The gradual evaporation of the water is taken care of by a constant level device at the opposite end from the condenser water inlets. The spent water from the condensers drains into this constant level device, and by this means sufficient

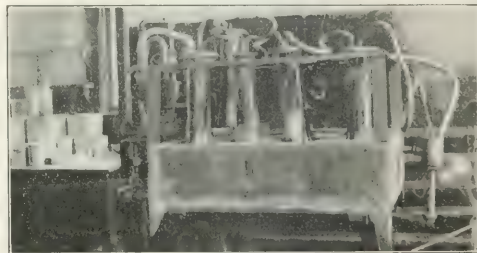


FIG. II

water is added automatically to replace that lost by evaporation. There is a draw-off at the bottom of the bath for cleaning purposes. The connections of the condensers are made with rubber tubing. The whole outfit can be placed on brackets on the wall with water and steam connections, and takes up but little space. A picture of one of these baths in use is shown in Fig. II.

The filter cups or thimbles are made of Schleicher & Schuell No. 575 hardened filter paper, which comes in cut circles. The size used is 15 cm. in diameter. To make a cup, two circles should be taken and one cut down to a diameter of about 14 cm. A round stick about one inch in diameter is used as a form. The stick is placed in the center of the circles of filter paper, the smaller inside; the papers are then folded symmetrically around the stick to form a cup of about  $2\frac{1}{2}$  inches in length. A very little practice enables the operator to make these evenly and quickly. After being made, they are soaked in benzol to remove any grease due to handling, drained, dried in a steam oven and kept in a desiccator until used.

Besides the apparatus previously described, the laboratory requires beakers, stirring-rods, carbon

filter tubes, and a weighing bottle, all of which are regular stock apparatus. A steam oven for drying is desirable, but an ordinary hot air oven can be made to take its place. A small camel's hair brush or stout chicken feather trimmed down to a fan at the end, should be available as a policeman for removing the last portions of the carbon from beakers.

#### ANALYTICAL PROCEDURE

If tar is to be assayed, it must be dried before testing, and after drying it is passed hot through a thirty mesh sieve to remove any foreign substances. Pitch requires no previous treatment, other than the ordinary procedure of insuring an average sample. If the pitch is hard enough, grinding the material taken for test will be advantageous in aiding the subsequent solution. In testing materials of 5 per cent or more carbon content, 5 grams should be taken for the test. With lesser percentages, 10 grams should be used. The amount is weighed out in a 100 cc. beaker, and digested with about 50 cc. of c. p. toluol on the steam bath for a period not to exceed thirty minutes. If the solution is kept hot and constantly stirred, the digestion can be completed very rapidly. A filter cup, prepared as described, is weighed in a weighing bottle and placed in a carbon filter tube over a beaker or flask. The toluol-tar mixture is now decanted through the thimble and washed with hot c. p. toluol until clean, using some form of policeman which is unaffected by toluol for the purpose of detaching any carbon which may adhere to the beaker. The cup is finally given a washing with hot c. p. benzol and then, after draining, is covered with a cap of filter paper or alundum, and placed in the extraction apparatus in which the c. p. benzol is used as a solvent. The extraction is continued until the descending benzol is colorless. The thimble is then removed, the cap taken off, dried in the steam oven, and weighed in the weighing bottle after cooling in the desiccator. The balance used for this work should be accurate to at least a half milligram. When pitches are being tested, it is well to examine the carbon residue for foreign matter, such as wood slivers, pieces of bagging, etc. If such foreign matter is present, the test should be rejected. All of the apparatus for this test, with the exception of the special water bath, can be obtained from the Arthur H. Thomas Company of Philadelphia, Pa. This water bath is only desirable if a number of such tests are run as routine work; for occasional tests it would not pay to have one made.

It is the hope of the writer that this paper will throw some light on the nature of "free carbon" in tar products, and that the procedure given here will be useful to the chemist who has occasion to test these materials. He would also express his appreciation of the work of Messrs. L. B. Shipley and C. R. Downs, who performed many of the tests and analyses which are recorded in this paper. One thing which must be kept in mind in free carbon tests as in other analyses of this nature, is that the results obtained are only proximate, and in order to obtain concordant results, faithful attention to details is necessary. We believe

that we have completely standardized all the essential conditions of the test considered, and that it can be applied successfully by workers in general.

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### THE RELATION BETWEEN THE MELTING POINT AND THE VISCOSITY OF REFINED TAR<sup>1</sup>

By PHILIP P. SHARPLES

The rough dependence of the viscosity of refined tars as determined by any of the standard instruments and their melting point has been long recognized. Many discrepancies have, however, been noted and apparently little thought has been given to the relation between the two in making specifications.

Table I shows a series of samples taken from refined tars made on a manufacturing scale from the same raw tars. The methods used in analysis are those described by S. R. Church in *THIS JOURNAL* 3 (1911), 227 and 5 (1913), 195.

TABLE I—A SERIES OF SAMPLES OF REFINED TAR MADE FROM SAME RAW TAR

Sample No.	Free carbon Percent-ages	Distillation total to 315° C.	Melting point ° F.	Schutte penetrometer Sec. at ° F.	Viscosity Engler 100 cc. at 100° C. Sec.	Float test at 50° C. Sec.
5	12.1	21.8		29 40	94	44
7	12.0	19.2		108 40	127	38
8	14.0	16.4		114 50	159	58
9	14.4	14.9	86.9	85 60	208	75
10	17.2	12.7	99.7	90 70	335	110
11	18.2	10.4	108.7	88 80	431	170

The melting point is the half-inch cube method in water, starting, however, at 40° F. instead of 60° F.

The Schutte penetrometer is, strictly speaking, not a penetrometer, but a modified melting point. An arbitrary melting point is assigned and the time taken at the assumed melting point to force out under constant pressure a plug of the material cooled to 40° F. is noted. The arbitrary melting point is so chosen on a 10° F. scale that the number of seconds is as near as possible 100.

The float test is the New York Testing Laboratory test. The plug was cooled to 41° F. before floating. The Engler test is made under standard conditions with the exception that 100 cc. were run off instead of 200 cc. The reduction of the number of cubic centimeters with viscous materials allows more concordant results to be obtained and gives lower figures.

A comparison of the three melting points and the Schutte penetrometer figures show that they advance quite regularly together. Other experiments have shown this same relation to hold true, provided the free carbon content is very nearly the same. Samples 7 and 8 may then be included in our further examination of the results without introducing undue error.

An examination of the float test shows an increasing interval between samples as we ascend in the series. Between 7 and 8 the interval is 20 sec. while between 10 and 11 the interval is 60 sec.

The results with the Engler viscosimeter show the

<sup>1</sup> Presented at the Atlanta Meeting of the American Association for the Advancement of Science, January, 1914.



same tendency much more accentuated. The interval between Samples 7 and 8 is 32 sec. while between Samples 10 and 11 it is 96 sec. It is interesting to note that the ratio is the same as in the float test.

A more careful consideration of temperature in testing tar materials with viscosimeters would seem to be indicated. The tars are more sensitive to temperature changes than oils or asphalts and not enough attention has been paid to viscosity changes with temperature.

The work in Table II was undertaken to show that although a specification was rather closely drawn for the Engler reading at 60° C., yet it failed in its object

TABLE II—COMPARISON OF MIXTURES OF TAR H AND TAR D ON ENGLER VISCOSIMETER—100 CC. AT THREE TEMPERATURES

Mixture Percentage		Free carbon estimated Percentages	Sec. at		
H	D		40° C	50° C	60° C.
40	60	4.4	75.7	54.6	41.0
50	50	5.0	88.1	57.6	45.6
60	40	5.6	97.3	62.5	47.0
70	30	6.2	110.5	66.3	48.7
80	20	6.8	136.1	83.3	56.0

in that it admitted all mixtures of tar H and tar D from 40 per cent H to 80 per cent H. Testing the same mixtures at 50° C. shows that the same limit in the upper part of the table would confine the mixture to within 20 per cent while at 40° C. the same limit would confine it to within 15 per cent.

The table also illustrates again the rapid increase in the time interval as the temperature of the determination of the viscosity approaches the melting point. Thus under 60° C. the space interval is 4.6 for the 50 per cent mixture H, but this is increased to 25.6 for the 80 per cent H mixture at 40° C.

The examples that have been cited have been in series of tars of nearly uniform composition. An illustration of the effect of free carbon on the relation between the melting point and the viscosity is given in Table III. The effect of the free carbon is very marked. In the Schutte and float test the times are markedly increased. With the Engler the results

TABLE III—REFINED TARS—RELATION OF VISCOSITY TO CARBON CONTENT

Sample No	Free carbon percentages	Melting point ° F	Schutte penetrometer at 80° F.	Engler 100 cc. at 212° F.		Float test at 212° F.
			Sec.	Sec.	Sec.	
1	1.4	110	42.2	302	158	
2	14.5	109	80.1	298	192	
3	39.6	112	144.9	739	337	

are more irregular, but show a marked increase with the high carbon tar. From a physical standpoint, the increase of free carbon might be expected to have this effect. It impedes the flow of the material with increase of temperature and in that way up to the point at which the free carbon tends to weaken the binding and lasting qualities of the tar, would seem to be a desirable addition.

The inclusion of both the melting point and the viscosity in a physical examination of refined tars to be used as binders would seem to be warranted. The viscosity at 100° C. compared with the melting point would give an indication of the behavior of the tar

with uniform distributors and also an indication of its resistance to temperature changes when used on the road.

#### CONCLUSIONS

I. The viscosities of tars of the same composition vary with the melting point, but not in direct ratio.

II. The viscosities of tars of the same melting point but of different carbon content increase with the carbon content.

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#### THE DIFFERENTIATION OF NATURAL AND OIL ASPHALTS

By E. C. PAILLER

Received November 11, 1913

The chemical knowledge of asphalts at the present time is undoubtedly very limited, the chemical tests used being mostly arbitrary ones. The lack of scientific analytical methods has perhaps never been felt more than at the present time. The asphalts used for paving purposes can be divided into two classes—natural asphalts, such as Trinidad and Bermudez asphalts, and oil asphalts obtained from asphaltic petroleum oil by means of freeing it from the lighter oils by distillation. It is considered impossible to identify mixtures of natural and oil asphalts, especially when such a mixture is made into an asphaltic cement, which is usually accomplished by fluxing the refined asphalt with maltha or other petroleum residuum. If the chemist has no means of detection, is it any wonder that the practice of substituting oil asphalt for natural asphalt exists?

In this paper the author wishes to be distinctly understood as neither recommending nor condemning the asphalts mentioned, but to find some means to identify the nature of them, pure and in mixtures. The test to date was simply to determine the fixed carbon content and mineral matter, and judging by the mineral matter, fixed carbon and physical tests, mixtures could be detected but only to a limited degree. It is well known how great a variation of mineral matter exists in all asphalts. The same is true of the fixed carbon content.

The following table shows the average, minimum and maximum amounts found:

	PERCENTAGES			FIXED CARBON			MINERAL MATTER		
	Av.	Max.	Min.	Av.	Max.	Min.	Av.	Max.	Min.
Trinidad.....	10.20	10.60	9.80	35.00	38.00	30.00?			
Bermudez.....	12.90	13.50	12.50	4.00	5.00	3.00			
California.....	14.50	16.00	13.80	0.15	0.20	Trace			
Mexican.....	15.50	18.00	13.50	0.20	0.30	Trace			

The foregoing shows that if we take a mixture of, say, 50 per cent Bermudez and 50 per cent California, it will, under conditions, be almost impossible to detect the presence of the California, for, assuming the fixed carbon content to be 12.50 per cent for Bermudez and 14.50 per cent for California, the 1:1 mixture will have a fixed carbon content of 13.50 per cent.

Much has been said for and against the fixed carbon

determination. Lester Kirschbaum<sup>1</sup> states that the fixed carbon content is a means of identification of native bitumens. It is true that the fixed carbon content in natural bitumens is clearly defined, the range being less than 2 per cent and therefore it is valuable as an indication as to the purity of the natural asphalts, even if they are fluxed. Should a Bermudez asphalt show a fixed carbon of 14 per cent or more, I would expect that the sample in question is not straight Bermudez and other tests described later would be made. If, however, a petroleum residuum is under consideration, the fixed carbon content as a means of identification is of not much value, although an important significance may be attached to it. Kirschbaum, in his article, treated this subject in an elaborate manner and it is quite logical to look upon the fixed carbon in oil residuum as an index of the severity of the heat treatment it has received. Unfortunately the fixed carbon in California, Mexican and Texas oil residuums may be the same for all and it is seen that it would be impossible to draw conclusions from this determination. The method employed in the fixed carbon determination is described in the *Jour. Am. Chem. Soc.*, **21** (1899), 1116. To test the accuracy of the method a sample was given to four different chemists, who were instructed to use the same method. The results obtained were as follows:

Percentages	Volatile combustible matter	Fixed carbon	Mineral matter
1.....	83.03	16.77	0.20
2.....	82.93	16.67	0.20
3.....	82.80	17.02	0.18
4.....	82.76	17.08	0.16

L. M. Law<sup>2</sup> quite recently had fixed carbon determinations made on two samples at six laboratories and the results obtained differed 6 per cent on one and 9 per cent on the other sample. However, three results in each sample check very well, and I am safe in saying that these three laboratories evidently employed the same method. The fixed carbon determination is an arbitrary one and has to be carried out to the smallest detail. The burners, crucible, size of flame, etc., have to be the same in all determinations to obtain the right results. Could anyone expect to get the same results if, in the sulfonation test, he would use dilute sulfuric acid, and in the other concentrated or in a moisture determination if he would heat the substance to only 50° C.? The pressure and the composition of the gas has very little effect on the result. This is shown on the three following tests: No. 1 was run with gas at full pressure, No. 2 with the same gas at reduced pressure and No. 3 with different gas and pressure at the author's private laboratory.

## PERCENTAGES FIXED CARBON

No. 1.....	16.87	No. 2.....	17.45	No. 3.....	17.08
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My contention is that a fixed carbon determination is of much value in asphalt analysis, in native bitumens as a means of identification and in petroleum residues as an index of the severity of heat treatment the

petroleum was subjected to—the former, however, only in conjunction with test described later.

Very little is known of the chemical composition of the bitumens contained in asphalts. They are hydrocarbons of complex structure, largely cyclic and bridge compounds, together with a small amount of their sulfur and nitrogen derivatives and are closely related to the hydrocarbons occurring in petroleum; as a matter of fact, some writers have advanced the theory that asphalts are the residue of petroleum, the lighter constituents of which have in a natural way evaporated.

The process to convert oil into asphalt, which took ages in nature, is used in the manufacture of oil asphalts, and is accomplished in a few days. The difficulty in distinguishing between the natural and artificial asphalts, or in proving their presence in a mixture, is due to this fact. Malencovic<sup>1</sup> states that oil asphalts and natural asphalts differ in that the former do not react with mercuric bromid solution; the latter, however, owing to their sulfur contents, give a precipitate. This test, however, is of no use, as oil asphalts are very often artificially sulfonated and consequently give the reaction. The sulfur content in oil asphalts and natural asphalts is, if the oil asphalt is not sulfonated, quite different, as the following table shows:

PERCENTAGES SULFUR			
Trinidad.....	4.35	California less than.....	2.0
Bermudez.....	5-6	Mexican.....	4.0

The sulfur content is determined by igniting the asphalt in an atmosphere of oxygen, precipitating the SO<sub>3</sub> with BaSO<sub>4</sub>. The ignition of asphalt in oxygen consequently oxidizing the sulfur to SO<sub>3</sub> is more accurate and easier to perform than the oxidation of the sulfur by the Carius method. A number of experiments have shown that it is quite difficult to oxidize all of the asphalt in some cases. In others it was found that the results were too high by the Carius method, to say nothing of the danger of exploding the glass tube. It is not at all unusual to have three or four tubes blown up in a single determination. The method, using Graef's apparatus, is easily performed, requires but little time and the apparatus used is moderate in cost.

As stated before, it is doubtful whether the determination of sulfur is of any practical value as an identification, as many oil asphalts are artificially sulfonated and some oil asphalts contain naturally a considerable amount of sulfur. Kast and Logan<sup>2</sup> state that all petroleum, and therefore petroleum residue, except that from Legernesee, contain sulfur (from 0.14-1.90 per cent). This sulfur may be present as free sulfur, sulfides or complex sulfur compounds. Mabery and Quayle succeeded in isolating a series of alkyl sulfur compounds by distilling crude Canadian oils at a pressure of 55 mm. Richardson and Wallace have found free sulfur to be the form in which the larger part if not nearly all of the sulfur in Texas oil exists. Some hydrogen sulfide is dissolved in the oil and a large amount is formed if the oil is heated as in

<sup>1</sup> Engineering and Contracting, Feb. 12, 1913.

<sup>2</sup> THIS JOURNAL, **6**, 1021.

<sup>1</sup> Baumaterialienkunde, **1906**, p. 29

<sup>2</sup> Jour. Soc. Chem. Ind., **19** (1900), 505.

distillation. The sulfur content in Mexican oil asphalt is as high as 6.20 per cent. Considering this fact, a sulfur determination alone would not amount to much as an identification of asphalts, especially mixtures or asphaltic cements which are fluxed with oil residuum.

J. Marcussen<sup>1</sup> states that in all natural asphalts there are present a number of organic acids or acid salts, which on distilling are collected in the first few cc. of the distillate and this distillate also contains a certain amount of saponifiable oils. It was this statement which was the basis of this investigation. There was, however, no method given as to the manner of distillation. The collecting of the distillate, and accordingly the results obtained in a rough-and-tumble way did, by no means, give satisfactory results and the first step was to devise a method which would, under the same conditions, give uniform results. The acids present are organic and are all insoluble in water. They are also not decomposed by heat and the test can safely be carried on at a temperature of 375° C.

The apparatus used is a small retort of 150 cc. capacity, two weighing bottles of 10 cc. capacity and two 8 oz. Erlenmeyer flasks. The reagents are *N*/10 NaOH, ethyl ether, neutral alcohol of 95 per cent strength and a 1 per cent alcoholic solution of alkaline blue.

#### METHOD

Thirty grams of bitumen or an amount of asphalt which will yield 30 grams bitumen are placed in the retort and heated until it melts. The flame is now raised until the first drop distills and so adjusted that about one drop in two seconds is collected. The distillate is collected in the weighing tubes (the weight of which were previously obtained) in 5 cc. portions and kept separate. After weighing the tubes with the oil, each of the distillates is dissolved in 10 cc. portions of ether. The ethereal solution is then washed with water in a separatory funnel until free from mineral acids which may be present, transferred to the Erlenmeyer flask, diluted with 75 cc. neutral alcohol, 5 cc. of the alkaline blue solution are added and titrated until the red color changes to blue. The acid number is expressed in milligrams of KOH used to neutralize the acid in 1 gram of oil distillate. The following table shows some of the results obtained:

BRAND OF ASPHALT	ACID VALUE	
	DISC. 1	DISC. 2
1 Pure Trinidad	16.20	8.40
2 Pure Trinidad	15.50	7.90
3 Pure Bermudez	9.80	3.20
4 Pure Bermudez	9.60	3.60
5 Pure California	0.11	0.07
6 Pure California	0.19	0.04
7 Maltha flux	0.12	0.25
8 Maltha flux	0.16	0.19
9 Bermudez maltha	9.80	2.30
10 MEXICAN	0.24	0.05
11 Mexican	0.22	0.09
12 Bermudez + California	4.90	1.20
13 Bermudez + Mexican	5.40	2.00
14 Bermudez + California + maltha	5.50	1.70
15 Bermudez + Mexican + maltha	5.15	1.22

The above table shows clearly that the acid values of natural asphalts are considerably higher than those of oil

asphalts. The second distillate in both Trinidad and Bermudez asphalts shows still some acid value, while in California the second distillate is almost free from acids. Therefore, if the acid value falls below 1.0 we can safely say that we are dealing with an oil asphalt or a mixture. If we deal with an asphaltic cement, which will be shown by taking the penetration, ductility and other physical tests, we should expect an acid value of not less than what is given under No. 9. If it is lower, we can expect to deal with a mixture.

The acid number is of great value as a preliminary test, to determine whether we deal with natural or oil asphalts or a mixture. It was also noted that the behavior of the asphalts in the retort, while distilling, indicates the nature of the asphalt. Dealing with natural asphalts we have, as soon as distillation starts, dense yellow fumes, emitting a strong sulfide odor, which are entirely absent in California and other oil asphalts. Oil asphalts, too, distill much easier than natural, but at a higher temperature.

Having ascertained the acid value of the asphalt, the next step was to determine the saponifiable quantity. Five grams of ash-free asphalt are dissolved in 30 cc. benzol. This is boiled with 50 cc. *N* alcoholic KOH under a reflux condenser. After cooling to room temperature, 250 cc. 95 per cent alcohol are added and the excess of alkali titrated back with *N* H<sub>2</sub>SO<sub>4</sub> using alkaline blue as an indicator. The end reaction is, in spite of the dark color of the solution, very distinct. The flask is now heated again on the water bath and more acid added if the red color reappears. This is to be kept up until the color remains blue. A blank determination is run alongside on the reagents used, to make allowance for the action of the alkali on the glass.

The following table shows the results obtained by the above method:

ASPHALT	SAPO. NO
Trinidad	40.0
Bermudez	28.0
California	12.0
Mexican	10.5
Maltha flux	8.0
Bermudez and California, 1 : 1	20.5
Trinidad and California, 1 : 1	26.0
Bermudez and Mexican, 1 : 1	19.7
Trinidad and Mexican, 1 : 1	24.9

The above shows very clearly the great difference between natural and oil asphalts. The difference of this constant enables one to tell not only the nature of the asphalt, but also give fairly accurate quantitative results.

It is interesting to note that in asphalts, there is such a great difference in these two constants—the acid and saponification value and undoubtedly a further investigation will reveal more distinguishing means between the various brands of asphalts.

The foregoing proves that there are a number of tests which are of great value as single tests. In conjunction with other tests they show conclusively the nature of the asphalt or mixture. Furthermore, if the flux is known a mixture of oil and natural asphalts can readily be recognized, as the following table shows.

<sup>1</sup> Chem. Ztg., 36, 84, 801.



No.	Fixed carbon	Mineral matter	Acid value		Sapon. value	Conclusion as to nature of asphalt
			1st Dist	2nd Dist		
1.	12.30	4.90	9.6	3.6	29.8	Bernudez
2.....	9.95	35.60	15.9	8.1	36.0	Trinidad
3.....	15.85	Trace	0.16	0.08	11.2	California
4.....	10.10	Trace	0.12	0.18	7.4	Malta California
5.....	14.60	2.21	4.9	1.2	19.3	Bernudez 1 : 1
6.....	14.15	2.94	4.7	0.9	22.0	California and Bernudez 3 : 7
7.....	16.87	0.20	0.24	0.05	9.8	Mexican
8	17.24	0.22	0.22	0.09	10.7	Mexican

In concluding, I wish to acknowledge my indebtedness to Dr. F. Kleeberg for his valuable advice.

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## CHEMICAL UTILIZATION OF SOUTHERN PINE WASTE

By M. C. WHITAKER and J. S. BATES

Received February 13, 1914

The utilization of waste resinous wood not fit for lumber is a problem of great economic importance. The representative species are the Douglas fir, the Norway pine and the western yellow pine of the Pacific slope, the long-leaf pine and the associated Cuban pine of the southeastern states, the less important digger, lodgepole, sugar and pinon pines of the West and the short-leaf and loblolly pines of the South.

The most abundant resinous wood and the most important industrially is the long-leaf southern pine, *Pinus palustris*. As is well known, this is the chief wood of the South Atlantic and Gulf States and constitutes over one-quarter of the total timber cut in the United States. It is estimated that the forest areas cover over 70 million acres and that the stand of long-leaf pine amounts to about 232 billion board feet.<sup>1</sup>

The utilization of this waste resinous wood is an increasingly important factor in the naval stores industry. The virgin forests which have supplied the world with turpentine and rosin from gum are disappearing at a rapid rate and the principles of conservation demand that the tapping and wasting of the living trees should be relieved as far as possible by the recovery of resinous products from the felled waste wood.

### COMPOSITION OF LONG-LEAF PINE

The constituents of economic value existing in long-leaf pine are the oleoresin and the wood itself. The products actually obtained from the pine depend on the methods of treatment.

The oleoresin varies widely in composition but its composition is fairly uniform; the volatile oils comprise approximately 20 per cent of the crude gum and colophony or rosin makes up the remainder. The volatile oils or "crude turps" yield from 60 to 80 per cent actual turpentine and from 40 to 20 per cent heavier oils known collectively as "pine oil." The turpentine in the wood consists mainly of  $\alpha$ -pinene with smaller amounts of  $\beta$ -pinene, dipentene, camphene and traces of other oils.<sup>2</sup> The pine oil is essentially

terpineol, with smaller amounts of borneol, fenchyl alcohol, limonene, cineol and other terpenes and related compounds. Gum turpentine issues from the sapwood of the living tree and consists almost entirely of pinene, whereas the volatile oils of the heartwood contain appreciable amounts of dipentene and heavier oils. The main constituent (80-90 per cent) of the rosin is believed to be abietic acid or its anhydride; unsaponifiable matter usually occurs to the extent of about 10 per cent.

The true wood, considered apart from oleoresin and moisture, is essentially lignocellulose, made up of 55-65 per cent stable cellulose,  $(C_6H_{10}O_5)_n$ , associated in a colloidal state with about 30 per cent lignin, a carbohydrate body approaching the empirical formula<sup>1</sup>  $C_6H_7O_5$ . The balance is made up of lower carbohydrates, chiefly pentosans and hexosans, and small amounts of protein and mineral matter. The moisture content of pine varies from about 5 per cent in very fat wood to 30-40 per cent or more in some classes of lean wood.

### CLASSIFICATION OF WOOD WASTE

It is estimated that at least 60 per cent of the tree is wasted in the manufacture of lumber.<sup>2</sup>

Sawdust, slabs and edgings represent about 35 per cent of the original tree. Sawdust is usually low in oleoresin since its fine state of division allows more or less volatilization of the turpentine and average saw lumber is lean. Slabs are available in large quantities and offer one of the most convenient sources of raw material. Their percentage of bark is of course very high and its removal is a problem to be considered. Furthermore, slabs come from the outer sapwood of the tree, where the oleoresin content is lowest. The richest slabs are those from the "box face" of trees which have been tapped for gum resins.

Forest waste amounts to about 25 per cent of the original tree. Large branches, tree-tops and occasional logs left by the lumbermen afford raw material in forms compact enough for handling. Stumps usually have a high oleoresin content and their utilization is of special importance in cases where the land is being cleared for agricultural purposes.

The most attractive class of forest waste is the "dead and down" material known as "lightwood." After a tree dies the bark and outer sapwood gradually decay and in five to fifteen years there is left a resinous log, which resists the natural processes of disintegration for long periods.<sup>3</sup> Lightwood is often charred by the ground fires which run through the pine forests.

### INDUSTRIAL PROCESSES

The processes now employed for recovering valuable products from resinous woods have already been adequately described in THIS JOURNAL.<sup>4</sup> The methods

<sup>1</sup> Klason, see Schwalbe, "Die Chemie der Cellulose," pp. 395 and 441. Dean and Tower, *J. Am. Chem. Soc.*, **29**, 1119; Cross and Bevan, "Researches on Cellulose, III."

<sup>2</sup> U. S. Dept. Agric., *Y. B. Sep.*, **534** (1910), 257.

<sup>3</sup> Tschirch in "Die Harze und die Harzbehalter" describes the progressive accumulation of rosin in a wounded or dead tree as a pathological process carried on by minute organisms.

<sup>4</sup> Herty, THIS JOURNAL, **5**, 65; Teeple, **5**, 680; French and Withrow, **6**, 148.

<sup>1</sup> U. S. Dept. Agric., Forest Service, Bull. **99**, p. 8.

<sup>2</sup> *Ibid.*, **119**, p. 7; Bur. Chem., Bull. **144**, p. 21.

differ rather widely in principle and yield a variety of end products. Turpentine orcharding provides high-grade turpentine and rosin by the tapping of living trees. Destructive distillation of rich pine yields turpentine, rosin spirits, rosin oils, tar oils, pitch, charcoal and other products. Steam distillation of shredded wood provides for the removal of only turpentine and pine oil. There has been some commercial success in extracting rosin and turpentine from resinous pine by means of volatile solvents, such as gasoline and naphtha. Rosin may also be dissolved by solutions of alkali. In some cases the volatile oils have been extracted by hot baths of non-volatile or high-boiling material, such as rosin, pitch, pine tar, etc. The hydrolysis of the lignocellulose complex of wood by dilute solutions of sulfurous, sulfuric or hydrochloric acids at elevated pressures and the production of ethyl alcohol from the fermentable sugars so formed constitute a problem of ever-growing interest.

The use of long-leaf pine for the manufacture of pulp and paper is an industrial development of recent years. Several plants are already in operation in the South and other extensive projects are under way.

The soda and the sulfate processes are preferred, while sound, lean wood is best adapted to pulpmaking. The large quantities of mill waste in the South offer a convenient and cheap source of raw material.

To make the treatment of the more resinous classes of pine waste profitable, attention must be given to by-products. Rosin and turpentine may be first removed by a volatile solvent.<sup>1</sup> Several of the methods suggested have aimed at preliminary removal of the volatile oils in a pure form by distilling at moderate pressures with steam alone<sup>2</sup> or in presence of alkali solutions.<sup>3</sup> It has been claimed that part of the rosin can be melted down and tapped from the bottom of the digester.<sup>4</sup> The spent pulping liquors may be evaporated and destructively distilled to yield rosin spirits, pyrolinegous acid, tar, etc.<sup>5</sup>

#### SCOPE OF INVESTIGATION

In the chemical utilization of resinous wood waste on a profitable commercial basis, it is essential to aim at simplicity of treatment and at the same time provide for a complete recovery of valuable products. Under existing processes one or more of the valuable constituents of the wood is usually impaired or sacrificed or the operations involve unusual or expensive difficulties. The minimum number of end products is a decided advantage and all processes must be simple and inexpensive.

It was with these considerations in mind that an investigation of resinous pine waste was undertaken. As excellent paper pulp had been made from long-leaf pine it seemed likely that a process might be perfected by which the most valuable products—turpentine, rosin and pulp—might all be recovered in marketable form. Since rosin is readily saponified

by alkalies and thereby rendered soluble in water, it was decided to make use of this principle in extracting the rosin from the wood. The fact that turpentine and pine oil are volatile with steam at temperatures far below their boiling points suggested making the preliminary extraction at low steam pressures, thus allowing separation of the volatile oils. After removal of the rosin and turpentine, the chips could be steamed with stronger alkali under pressure, for the production of paper pulp.

In addition to the investigation of the factors affecting such a treatment of the wood, it was important to determine the quality and yields of the products and to provide for their purification.

There have been a number of suggestions for the utilization of resinous materials involving the principle of alkali extraction.

Craighill and Kerr<sup>1</sup> patented a process by which chipped wood is treated first with a small volume of liquor containing an amount of caustic soda "just sufficient to saponify the rosin and oils and neutralize the (volatile) acids without dissolving the other extractive matters of the wood." Steam is admitted long enough to distil the terpenes; water is then added to submerge the chips in alkaline solution, and steaming is continued until saponification of rosin is complete. The solution is then drawn off and the chips treated with a stronger caustic solution for the production of paper pulp.

J. Aktschourin<sup>2</sup> provides for the extraction of resinous material by heating with dilute alkali below 100° C. at several atmospheres pressure. The lower temperature lessens the attack of the lignin. The liquor is drawn off and cooled to precipitate a certain amount of emulsified resin and rosin soap. The filtrate is used in digesting the fibrous material at high steam pressure for pulp.

Where turpentine is the only product desired, alkali has, in some cases, been added primarily to disintegrate the rosin and thereby permit a more nearly complete distillation of the volatile oils.<sup>3</sup>

Kerr<sup>4</sup> has suggested a continuous process for the removal of turpentine and rosin from wood, the turpentine being first distilled with steam and the rosin being subsequently dissolved in alkaline liquor.

#### PRELIMINARY EXPERIMENTS

From a shipment of assorted pine waste, the "box-face slab" material was selected as being best suited to a laboratory investigation. This wood was sound and clean, and very rich and uniform in oleoresin content. When reduced to chips or shavings the wood had a strong turpentine odor and burned freely with a characteristic, smoky flame. Box-face slabs constitute a comparatively expensive and restricted source of raw material for commercial supply and the oleoresin content (30-40 per cent) is higher than that of average lightwood (15-25 per cent). This material, then, should present perhaps the severest conditions

<sup>1</sup> Rowley, U. S. Pat. 942,106.

<sup>2</sup> Hough, U. S. Pat. 903,859.

<sup>3</sup> Craighill and Kerr, U. S. Pat. 817,960.

<sup>4</sup> Saylor, U. S. Pat. 1,004,473; Hoskins, U. S. Pat. 770,463.

<sup>5</sup> U. S. Dept. Agric., Bur. Chem., Bull. 159.

<sup>1</sup> U. S. Pat. 817,960, April 17, 1906.

<sup>2</sup> French Patents 432,998, Aug. 5, 1911, and 433,424, Aug. 11, 1911, Ger. Pat. 248,275, July 12, 1912, and 257,015, Jan. 12, 1913.

<sup>3</sup> Hough, U. S. Pat. 903,471.

<sup>4</sup> U. S. Pat. 832,863.

for complete extraction of rosin and turpentine, but the yields must be considered a maximum for southern pine waste.

Sample slabs were carefully cleaned by the removal of bark, rosin "scrape" and other surface material. Only the clean, inside wood was used in the investigations. Some of the wood was reduced to large chips—about 1 in.  $\times$   $\frac{3}{4}$  in.  $\times$   $\frac{1}{8}$  in.—some to small chips—about  $\frac{1}{2}$  in.  $\times$   $\frac{1}{4}$  in.  $\times$   $\frac{1}{32}$  in.—and another portion to thin shavings.

A number of preliminary extraction experiments were made to determine the action of caustic soda and sodium carbonate on the wood under various conditions of temperature and pressure. In general, caustic soda seemed to be the more effective reagent for rosin extraction. Sodium carbonate gave cleaner extracts by reason of its milder attack of the lignocellulose, but penetration of the wood was in most cases incomplete. Elevated temperatures and pressures facilitated the removal of rosin and turpentine, but occasioned greater attack of the wood itself. Vacuum treatment proved unsatisfactory, due to slow penetration of the alkali into the wood at the lower temperatures and to the tendency toward frothing, especially while turpentine distillation was proceeding most rapidly. The size of wood unit proved to be a highly important factor in extraction of the oleoresin. A fine state of division, represented by the shavings, greatly simplified the problem of extraction. On the other hand, the production of good paper pulp necessitates the preparation of the wood in chip form and this introduced some complication in the preliminary alkali treatment.

The brown extracts obtained by heating the resinous wood in dilute caustic solutions consisted mainly of sodium resinate and the sodium salts of humic acids. Isolation of the rosin content of the alkali extract was accomplished by salting out the rosin soap with caustic soda. Humus itself is soluble in alkaline solution but a small part is carried down by the colloidal soap. Sodium resinate is quite soluble in hot alkaline solutions, as well as in neutral or faintly alkaline solutions in the cold, but is only slightly soluble in cold alkaline solutions when the concentration of free caustic soda exceeds about 4 per cent. This solubility determines the loss in recovery of the soap.

The method has the advantage of utilizing the same reagent for salting out as is employed for extracting the wood and cooking for pulp. No acid is necessary for precipitating the free rosin, if the soap is to be used as such, and no acid-resisting apparatus need be provided. The alkali used in extracting the wood and precipitating the soap can be saved partly in the form of sodium resinate (thereby enhancing the value of the rosin fraction), and partly in the form of brown, supernatant liquor to be used as a source of alkali for the soda cook of the extracted chips. After the pulping operation, the alkali can be recovered in the usual way by evaporating, incineration and causticizing the waste soda liquor.

As regards actual manipulation, it was found best to add the excess of caustic soda to the hot extract, so that precipitation of the soap took place rather

slowly as the solution cooled down. Very strong alkali—above 10 per cent NaOH—gave somewhat syrupy solutions, with increased contamination of the soap by humus and without appreciable gain in the quantity of soap precipitated. The soap precipitate proved difficult to filter and was separated by draining or syphoning. With this procedure the soft precipitate retained an appreciable quantity of liquor. The bulk of the humus was removed from the soap by dissolving the same in the minimum amount of hot water and salting out again with caustic soda.

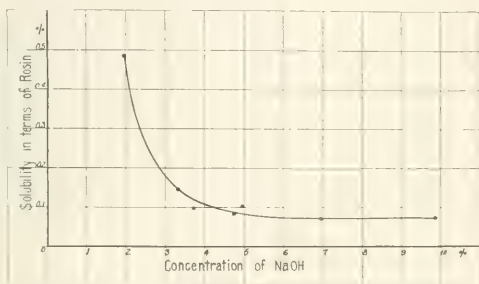


FIG. 1. SALTING OUT CURVE

SOLUBILITY OF ROSIN IN SODIUM RESINATE IN NaOH SOLUTIONS AT 20-25°C

To determine the power of caustic soda in salting out rosin soap, a series of experiments was carried out with pure rosin on a quantitative scale. The results are summarized in Fig. 1.

#### PRACTICAL EXPERIMENTS

Experiments were undertaken on a larger scale to approach more closely the conditions in actual commercial operation. The wood was prepared in the form of chips of the ordinary pulping size, then subjected to a mild preliminary steaming in dilute alkali to recover the rosin and turpentine, and finally cooked in stronger alkali in the usual way for pulp. The preliminary extraction was studied to determine the conditions for complete solution of the rosin and simultaneous distillation of the turpentine. The draining of the alkali extract from the chips and the salting out of the rosin soap by subsequent addition of excess caustic soda were carried out with conservation of alkali in mind, as well as high recovery of rosin soap. The second stage of the process—the production of pulp from the extracted chips—was carried through to note any possible deleterious effect of the preliminary steaming on the quality or yield of the final pulp. The experiments were designed to throw light on the problem of commercial feasibility.

The wood studied was limited to box-face slab material, reduced to chips by sawing into short lengths and splitting to an average size of about  $1\frac{1}{8}$  in.  $\times$   $\frac{3}{4}$  in.  $\times$   $\frac{3}{32}$  in. These chips were considerably longer than the smallest commercial size and, as penetration of wood proceeds most readily along the grain, the conditions for alkali extraction were certainly as severe as industrial practice would necessitate. The main supply of chips was thoroughly mixed and representative samples obtained for analysis by quarter-



ing and subdividing. The chips were stored in stoppered jars to prevent loss of turpentine, while the samples were used to determine the composition of the wood.

#### ANALYSIS OF THE CHIPS

The rosin content was determined by extracting 25 gram portions of the very fine chips with ether in a Soxhlet. On drying the chips at 105° C. after extraction with ether, a figure was obtained representing the percentage of "actual wood"—free from moisture, turpentine and rosin. This value has been used in computing the true pulp yields. The percentage of volatile oils could not be accurately determined on a small scale, so the highest yield obtained in the subsequent steaming experiments has been taken as a close approximation of the true "turpentine" content of the wood. In Expts. 5 and 6, 1500 grams of wood yielded 145 cc. of "turps" weighing approximately 126 grams on the basis of 0.87 specific gravity. This shows that the wood contained close to 8.4 per cent by weight of turpentine and pine oil.

The average composition of the wood supply was found to be as follows:

	Percentages
"Actual wood".....	54.3
Rosin.....	32.1
Volatile oils.....	8.4
Moisture, by difference.....	5.2
	100.0

Thus, the total oleoresin amounted to 40.5 per cent, made up of 79.2 per cent rosin and 20.8 per cent volatile oils.

#### APPARATUS

The digester used in carrying out the extraction and cooking of the wood was made from an extra-heavy cast iron tee, 6 in. X 6 in. X 4 in. The apparatus was supported in a horizontal position by resting the flanges in two concrete yokes. The 4 in. outlet of the tee was turned upward to act as a dome for the collection of steam and turpentine vapor; this arm was also used for charging and discharging. The digester was equipped with thermometer pocket, pressure gage and relief line, controlled by a needle valve and leading to a glass condenser. An internal stirring device, consisting of a small shaft fitted with arms, allowed mixing of the contents of the digester when desired. As condensation was too great when the digester was heated by live steam, heat was furnished by two gas burners.

The manipulation was much the same in all the experiments. For the preliminary extraction, from one to two kilograms of resinous chips were placed in the digester and covered with a measured volume of alkaline liquor, containing the desired amount of NaOH or Na<sub>2</sub>CO<sub>3</sub>. Space had to be left for steam collection on account of the tendency toward foaming. The top flange was then securely bolted in place, all necessary connections were made and the burners started. In about an hour the relief line was opened to permit steam distillation of the volatile oils. The burners were controlled to maintain a fixed, low pressure (between 15 and 30 pounds) for extraction of the rosin.

Agitation was carried on continuously or intermittently to prevent local overheating and to facilitate solution of the rosin. Continuous stirring tended to fray the chips and render them less suitable for pulping.

The turpentine fractions were in most cases isolated every fifteen minutes during the relieving period. Figs. 2 and 3 show the rate of evolution of the volatile oils and the changes in refractive index and specific gravity during the course of distillation. After the

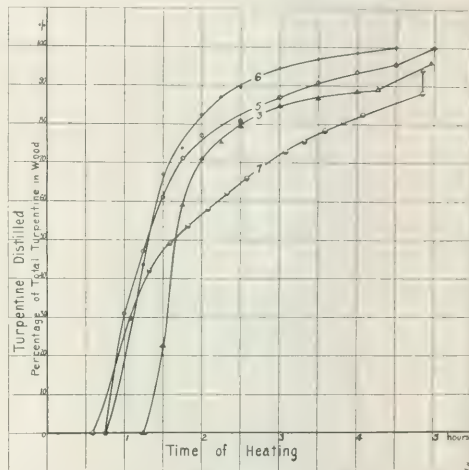


FIG. 2 RATE OF CRUDE TURPENTINE DISTILLATION DURING PRELIMINARY STEAMING

preliminary treatment no longer yielded turpentine in measurable amounts, the burners were removed and the pressure diminished. The digester was then inverted by rotating in its seat and the hot liquor drained through the relief line.

The "direct extract" was dark brown in color and the rosin was in perfect solution. For analytical purposes the liquor was aliquoted, which presented some difficulties. The liquor had to be kept hot to prevent precipitation of the rosin soap and the syrupy solution was not easy to handle. Some of the aliquot portions were strengthened, while hot, with additional caustic soda to make the precipitation of resinate more nearly complete. On cooling, the direct extract gave bulky precipitates of fairly white rosin soap. The dark supernatant liquors were decanted, drained through cotton or filter paper and analyzed for unprecipitated rosin. The soap, more or less contaminated with humus and liquor, was dissolved in water and the rosin determined in the usual way.

The chips retained from 1 to 1.5 times their weight of liquor after draining. This represents a serious loss of rosin. In order to recover most of this soap, the chips were washed by covering with hot water and boiling for some time. The "first wash liquor" was drained as before, cooled and aliquoted for determination of rosin content. The color of the solution was dark brown. No soap precipitated on cooling, al-

though about 90 per cent could be precipitated by caustic soda.

To further clean the chips enough to allow sampling and careful examination, the wood was washed a second time by boiling with fresh water. This "second wash liquor" contained but little rosin. In actual practice the chips would be ready for the introduction of pulping liquor after draining the first wash liquor from the digester.

The extracted chips after washing as above were discharged from the digester and allowed to dry somewhat. The chips had been appreciably softened by the alkali and darkened by partial attack of the lignin. After thorough mixing, the weight was taken and the mixture sampled. The sample was reduced to small chips and boiled with successive portions of water to remove the last traces of sodium resinate. This final washing yielded small amounts of rosin soap. The chips were then dried in the oven and extracted with ether to determine the percentage of unsaponified rosin left in the wood. This indicated the efficiency of the alkali extraction.

where preliminary extraction of the rosin had been incomplete.

At the end of the cook, the pressure was drawn down, the hot liquor drained off and the pulp washed thoroughly. To determine the yield, the pulp was pressed by hand, carefully sampled, and the aliquot portion dried at 105° C. The pulp was refined in a small beater, samples being taken at intervals and made into sheets on a hand frame.

Table I contains most of the important data bearing on the preliminary extractions. The rosin determinations have been reserved for later discussion. (See Table II)

In computing turpentine yield, a factor was worked out for the transformation of volume in cubic centimeters to gallons per cord. A yield of 1 cc. from 100 grams of wood is equivalent to a production of  $4000 \div (100 \times 8.335) = 4.8$  gallons from a cord of 4000 pounds. The wood used probably weighed considerably more than 4000 pounds per cord, but this figure has been chosen as a conservative estimate for rich pine.

TABLE I—PRELIMINARY ALKALI EXTRACTION OF RESINOUS CHIPS

ALKALI USED	SODIUM HYDROXIDE—NaOH						SODIUM CARBONATE Na <sub>2</sub> CO <sub>3</sub>
	EXPERIMENT NUMBER	1	2	3	4	5	6 <sup>(a)</sup>
Weight of resinous chips, grams	2000	1000	1000	1500	1500	1500	1500
Na <sub>2</sub> O used, multiple of theoretical value	3.2	1.6	2.17	4.34	3.47	3.0	3.26
Volume of liquor, cc.	7000	6000	5000	7000	7000	7150	7000
Strength of liquor, per cent Na <sub>2</sub> O	2.6	0.77	1.25	2.68	2.14	1.82	2.02
Relieving pressure, pounds gage	20	30-40	25-30	25	15-20	15-20	30
Time under pressure, hours	3.5	3.0	4.0	3.75	4.0	3.5	3.5
CRUDE TURPENTINE							
Cubic centimeters	113	86	93	139	145	145	128
Gallons per cord (4000 lbs.)	27.1	41.3	44.6	44.5	46.4	46.4	41.0
Index of refraction at 15° C.		1.4742	1.4742	1.4738	1.4738	1.4733	1.4742
Specific gravity at 15° C.		0.8753	0.8854	0.8849	0.8743	0.8770	0.8774
Dry, extracted chips (rosin-free), per cent of original wood			44.8	41.2	40.8	41.7	48.1
"Humus," dissolved, per cent of actual wood			17.5	24.1	24.8	23.2	11.4

(a) Extraction of smaller chips.

The sample of chips was finally dried at 105° C. and weighed giving the percentage of dry, rosin-free wood. The difference between the true wood content of the original resinous material and the weight of the wood after alkali extraction showed the extent of decomposition of the lignocellulose.

The second stage of the treatment was the production of pulp from the wood. The main portion of the chips, after alkali extraction and washing, was returned to the digester for the soda cook. Caustic soda solution was added to cover the chips and provide amounts of Na<sub>2</sub>O varying from 15 to 35 per cent of the weight of the wood.

A gage reading of 100 pounds was reached in 1-1/2 hours. The pressure was held at this arbitrary value for about three hours to obtain satisfactory disintegration of the wood. The preliminary treatment had already dissolved some of the lignin, so the final cooking was comparatively short.

The contents of the digester were agitated by stirring frequently. Distillation was carried on at intervals to detect any further evolution of turpentine. Only a few drops were obtained, except in those cases

The important variable in the various runs was the ratio of alkali to wood. The unit basis for calculating the amount of NaOH or Na<sub>2</sub>CO<sub>3</sub> to be used in the preliminary treatment was the weight of Na<sub>2</sub>O theoretically necessary to saponify the rosin in the wood. Although abietic acid has a molecular weight of about 312, American rosin<sup>1</sup> acts as if its "molecular weight" were close to 346. Of course, each sample of rosin has its own saponification number, but for convenience the latter figure above has been taken as an approximation of the average combining weight of the rosin in the chips. On this basis rosin would require  $31 \div 346 = 8.96$  per cent of its weight of Na<sub>2</sub>O to produce a neutral sodium resinate. The wood under consideration contained 32.1 per cent of rosin, so that 100 parts of resinous wood required at least 2.88 parts of Na<sub>2</sub>O for complete saponification of the rosin therein. The amounts of Na<sub>2</sub>O actually used have been expressed as multiples of this unit value. The attempt was to find the least amount of caustic which would completely extract the rosin before neutraliza-

<sup>1</sup> Lewkowitch, "Chemical Technology and Analysis of Oils, Fats and Waxes," Vol. I, p. 499.

tion, under conditions allowing efficient turpentine distillation and still preventing undue attack of the wood itself. With the preliminary extraction continued for 3.5 to 4 hours under 15 to 30 pounds pressure, the lower limit for NaOH was found to lie somewhere between 2.17 and 3.0 times the theoretical amount of caustic (see Expts. 3 and 6). In the former case extraction was incomplete, due to premature neutralization of the caustic, while in the latter there was thorough penetration of the wood and an appreciable excess of NaOH was found in the black liquors. Under the conditions employed, the minimum amount of caustic necessary for extraction could be safely placed at about 2.5 times the theoretical value. The excess above that needed for saponification of the rosin was of course neutralized by combining with the decomposition products from the wood itself.

The relieving pressure was varied somewhat, but without appreciable change in the other steaming factors. The aim was to discover the lowest pressure at which distillation of turpentine and penetration of the wood could be carried on without unduly lengthening the time of treatment. To attain least contamination of the rosin extract by the decomposition products of the lignin, it seemed desirable to work toward a low alkali ratio and a low steaming pressure. A pressure of 15-20 pounds was found to be most effective.

The time consumed in extraction varied from 3.5 to 4 hours and must, in most cases, be considered a maximum, because of the attempt to recover all the turpentine. The greater proportion of the run was spent in distilling the last small portions of oil. An important feature in the design of a digester for practical operation would be the provision for rapid steam distillation, so that the final portions of volatile oil could be carried over as soon as liberated by disintegration of the rosin. This would shorten the time of preliminary treatment and decrease the effect of the alkali on the rosin and the wood. A large dome or distilling head set with closed steam coils might successfully break the froth and allow proper control of distillation from the digester.

There was considerable attack of the lignocellulose, as may be seen from the amounts of humus, etc., dissolved (11.4-24.8 per cent of the actual wood). This decomposition of lignin seemed to depend as much on the time of contact with the alkali as on the strength of caustic used. This action does not signify a waste of alkali or an injury to the wood, but rather represents the first stages of the ordinary pulping operation. The dissolving of the humus is objectionable only because of its contamination of the rosin soap and of the extra steps involved in its removal.

Representative curves showing the rates of turpentine distillation are given in Fig. 2. In order to compare the results on a convenient basis the yields from Expts. 5 and 6 have been taken as standard and assumed to be 100 per cent of the volatile oils in the wood. All turpentine fractions in the four experiments considered have been calculated as percentages of this maximum value. The abscissas rep-

resent the total time of heating, starting from room temperature. The ordinates show the percentages of the total turpentine in the wood, which were recovered at different stages of the steaming.

The most noticeable feature of the curves is that the great bulk of the turpentine was recovered during the first stages of relieving and about as fast as the steam could carry it over. After relieving one hour, approximately 75 per cent of the turpentine had been recovered. The last 25 per cent was evolved more slowly. With proper appliances for more rapid distillation of steam, it is quite probable that this proportion of the turpentine could be recovered in much less time. The final upward turns of the curves represent the last fractions which were carried over by the rather large quantities of steam drawn off in reducing the pressure to atmospheric. The curve for Expt. 7 shows the retardation when sodium carbonate

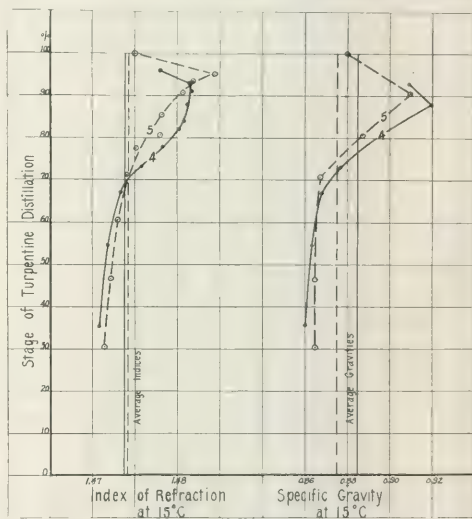


FIG. 3. CHANGES IN INDEX OF REFRACTION AND SPECIFIC GRAVITY OF CRUDE TURPENTINE DURING PROGRESS OF DISTILLATION

was used. The extraction of rosin was in this case incomplete. The vertical portion of the curve indicates the turpentine fraction recovered during final cooking for pulp.

Another feature is the remarkable similarity of the curves, in spite of the differences in treating the wood. In the three experiments where caustic soda was used, it will be seen that the curves almost converge at the two hour mark. This indicates that it makes little difference whether distillation is begun as soon as pressure is evidenced or whether relieving is postponed a little.

The gradual flattening of all the curves and the marked retardation in turpentine evolution in Expt. 7, where solution of the rosin was slow and incomplete, indicate pretty clearly that disintegration of the rosin is necessary for efficient turpentine recovery. This is the difficulty experienced in the



ordinary steam distillation process where the fine resinous material must be subjected to the action of steam for 3 to 10 hours and even then without the recovery of the last traces of oil. In a degree, then, the curves represent the speed of alkali penetration of the wood.

The amounts of steam necessary to carry over the various turpentine fractions are important from a practical view-point. In nearly all cases the first 50 per cent of the oil was distilled with less than its own volume of condensed water-vapor. The next 25 per cent required from 1 to 4 times its volume of aqueous distillate, the ratios in the most representative experiments (4, 5 and 6) being 1.2, 1.3 and 1.0, respectively. The fraction from 75 to 90 per cent required a ratio of 7-10 under properly regulated conditions. The figures for the final 10 per cent are not significant, because of the large amount of steam removed at the end of the treatment to ensure evolution of the last traces of turpentine. The ratios for this period varied from 40 to 50. It will be apparent that the ratios of condensed water vapor to turpentine are well within the practical limits. In fact, a much more rapid evolution of steam would be justified in order to shorten the steaming period.

The nature of the turpentine curves suggests that it might be found more economical in practice to discontinue the preliminary steaming before the last traces of turpentine were removed. This would mean a saving in steam consumption and a less severe attack of the wood itself.

It seems reasonable to assume that a properly conducted alkali extraction will allow recovery of all the volatile oils in the wood in a high state of purity.

Fig. 3 serves to show certain changes in the nature of the volatile oils during the progress of distillation. The fractions were saved separately every fifteen minutes in Expts. 4 and 5 and the refractive indices and specific gravity constants of each fraction determined. The ordinates have been chosen to represent the various stages of turpentine distillation, expressed in percentages of the total turpentine content of the wood. The backward turn at the end of each curve is occasioned by the final fraction obtained while diminishing the pressure. The average constants, obtained by finally combining all the fractions, are shown by the vertical lines.

The curves of index of refraction and specific gravity for a single experiment follow closely parallel to one another. Moreover, the curves are materially the same for the two experiments. It is apparent that the oil became heavier as distillation proceeded and that the last period of steaming was spent in removing the fractions which approach pine oil in general properties. This shows that distillation of the crude turpentine is not coincident with its liberation from the resin, for otherwise the distillate would be uniform throughout the run. The heavier constituents are carried over more slowly by the steam and require extended treatment to ensure their recovery. This also points to the advantage of rapid steam evolution during the last stages of the preliminary treatment, in order to remove

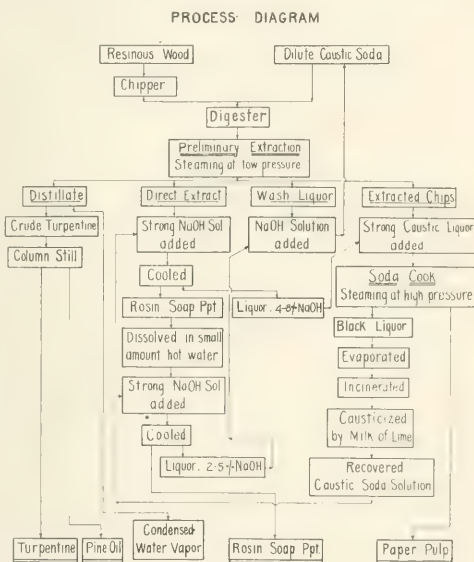
the heavier oils from the solution as quickly as possible.

The change in the nature of the oil during distillation suggests that this direct recovery might be used as a preliminary fractionation of the crude turpentine into "wood turpentine" and "pine oil."

#### RECLAIMING OF ROSIN

Table II shows the distribution of the rosin content of the wood after alkali extraction and washing. The analytical results have been expressed as percentages of the total rosin in the original wood as determined by extraction with ether.

As already mentioned, the direct extract was aliquoted and treated in two ways: some portions were allowed to cool directly; others were treated with additional caustic soda to precipitate the soap more completely and leave a supernatant liquor, which would



represent a solution available for the final soda cook in industrial practice. Where solution of the rosin was complete, from 75 to 79 per cent was removed in the first draining. Of this amount, from 96 to 97 per cent was recovered in the form of soap precipitate by strengthening the liquor with caustic soda up to 6 to 8 per cent. The sodium resinate remaining in solution was, of course, dependent on the solubility of the soap in the strong alkali and on this account was practically a constant quantity—2.3 to 2.8 per cent of the total. The percentage would be relatively higher in the case of leaner woods, but the actual loss is comparatively small. This unrecovered rosin would be carried through the soda cook and would be of some advantage as fuel in the final incineration involved in the recovery of alkali from the waste pulping liquors.

The figures for direct cooling of the extract are

interesting only in showing the necessity of salting out the soap with stronger caustic. The filtrate losses were high and varied inversely as the excess of alkali left in the extract after preliminary steaming. In Expt. 6, for instance, where the caustic was nearly all neutralized, the rosin remaining in solution amounted to 20.2 per cent of the total.

From 10 to 12 per cent of the rosin was removed in the first washing of the chips. This treatment must, therefore, be looked upon as an important step in the process. It was found that 80 or 90 per cent of this rosin soap could be recovered by precipitation with caustic. An industrial cycle might involve the salting out of the resinates in this way. An alternative would be the addition of enough caustic soda to the first wash liquor to allow its use directly as the alkali liquor for extraction of the wood in the succeeding cycle. This would permit the precipitation of the inherent resinates in the next "direct extract."

From the direct extract and the first wash liquor it was possible to recover about 85 per cent of the total rosin in the wood, in the form of rosin soap precipitate salted out of solution by means of caustic soda.

was the black liquor from the preliminary extraction of rosin, which had been strengthened with caustic soda to salt out most of the resinates. The sulfate process would have yielded better fiber, but there seemed no necessity of complicating the treatment by the addition of sodium sulfide.

In the first seven experiments, the chips which had been subjected to alkali extraction and washing were used as raw material. In Expt. 8 a single steaming of the wood was employed. The pressure was held at about 30 pounds for 3 hours in order to disintegrate the rosin and to distil the turpentine without decomposing it. The pressure was then raised to 100 pounds for final pulping.

The first two ratios—liquor : wood and  $\text{Na}_2\text{O}$  : wood—are based on the dry weight of the extracted chips in Expts. 1-7 and on the weight of the original resinous wood in Expt. 8. "Causticity" refers to the percentage of sodium oxide present in the cooking liquor in the form of  $\text{NaOH}$ , based on the total amount present both as  $\text{NaOH}$  and  $\text{Na}_2\text{CO}_3$ .

The pulp was dried at  $105^\circ\text{C}$ . and the yield calculated: *first*, as percentage of the original resinous wood to show the over-all yield; *second*, as percentage

TABLE II—DISTRIBUTION OF ROSIN AFTER ALKALI EXTRACTION

RESULTS IN PERCENTAGES OF TOTAL ROSIN IN ORIGINAL WOOD AS DETERMINED BY EXTRACTION WITH ETHER: TOTAL ROSIN = 32.1 PER CENT						
	EXPERIMENT NUMBER	3	4	5	6(a)	7(b)
Direct extract, direct cooling	{ soap precipitate	48.2	70.7	65.5	59.2	53.3
	{ filtrate	18.0	5.9	8.7	20.2	8.4
Direct extract, strengthening to 6 to 8 per cent NaOH	{ soap precipitate	63.5	75.0	72.0	76.5	59.5
	{ filtrate	2.7	2.8	2.8	2.8	2.3
Direct extract, total rosin as soap		66.2	77.2	74.5	79.4	61.7
First wash liquor, soluble rosin soap		11.7	10.6	11.2	9.7	10.0
Second wash liquor, soluble rosin soap		2.9	3.4	2.5	2.9	4.4
Washed chips, unsaponified rosin		7.8	0.15	0.9	0.14	8.0
Balance (by difference)		11.4	8.6	10.9	7.9	15.9

(a) Extraction of smaller chips with  $\text{NaOH}$ .(b) Extraction of larger chips with  $\text{Na}_2\text{CO}_3$ .

Comparatively little rosin was obtained from the second wash liquor and this step would hardly be justified in practice.

The unsaponified rosin, determined by ether extraction of the washed, dried chips, indicates the efficiency of the alkali extraction. In Expt. 3, 7.8 per cent of the rosin was left undissolved by reason of the premature neutralization of the small amount of caustic used. In Expt. 7 the sodium carbonate failed to penetrate the wood in the time allowed for steaming and 8 per cent of the rosin was retained in the free state by the chips. Expts. 4, 5 and 6 represent practically perfect extractions of rosin.

The "balance" includes 3 to 5 per cent of soluble resinates retained by the chips after the two washings and small quantities of soapy liquor surging over with the distillate during steaming. Mechanical losses in handling the liquors and in analysis are also involved in this figure. The main discrepancy seems to be due to decomposition occasioned by the alkali in dissolving the more or less complex resinous content of the wood.

#### PRODUCTION OF PULP

The more pertinent data on the soda cooks have been assembled in Table III. For the sake of convenience, caustic soda was used in reducing the wood to pulp. In Expt. 5 the solution used for cooking

of actual dry resin-free wood in the original material, to indicate the true efficiency of the pulping operation.

The turpentine figures refer in the first 7 experiments to the additional recovery during the soda cook, signifying, in several cases, incomplete disintegration of the oleoresin in the preliminary treatment. In Expt. 8 the turpentine was obtained by a combined extraction and pulping of the wood.

The actual data are, in many ways, not comparable with those in ordinary soda-mill practice. The "liquor : wood" ratio is usually from 4 to 6, when a digester is filled with chips and flooded with liquor. Because of the decreased volume of the wood after preliminary extraction, a larger ratio of cooking solution was necessary to properly fill the experimental digester and prevent exposure of the chips. With lean woods the  $\text{Na}_2\text{O}$  percentage is usually from 17 to 25 and the actual consumption of  $\text{NaOH}$  about 15, equivalent to about 11 per cent  $\text{Na}_2\text{O}$ . By reason of the partial attack of the lignin in the preliminary extraction, an amount of sodium oxide below 20 per cent was found to be most satisfactory. The above considerations necessitated a low strength of cooking liquor—lower than would be necessary in practice. A concentration of 5-10 per cent  $\text{NaOH}$  is usually employed in practice.

The pressures used in soda cooking vary from 75 to 150 pounds, the higher values applying particularly to deciduous woods, such as poplar and basswood. In these experiments a pressure of 100 pounds was chosen as a satisfactory figure for pine. The time necessary to reduce the pine to pulp was comparatively short, due to partial decomposition during preliminary steaming and also to the more effective action in the small digester.

The outstanding feature of the several experiments was that there was no failure in obtaining strong, long-fibered pulp of good quality. The preliminary extraction did not detract in any noticeable degree from the quality of the final fiber. The soundness of the raw material and the use of large chips was, of course, largely responsible for the favorable nature of the pulp. In Expts. 2, 3, 4 and 8, the pulp was quite thoroughly disintegrated by the stirring device and the fiber was "soft." It will be seen that low yield is coincident with soft fiber. In Expt. 5 the pulp retained the chip form, but yielded to disintegration on handling. Expt. 6 gave a strong pulp from the smaller chips. Expt. 7 represents a "raw" cook, in which the pulp was blown in the form of firm chips. Careful reduction in the beater gave a fiber of dark brown color and considerable strength, although the insufficient cooking had left the fiber somewhat "woody."

TABLE III SODA COOKS FOR PAPER PULP

	EXPERIMENT NUMBER							
	1	2	3	4	5 <sup>(a)</sup>	6 <sup>(b)</sup>	7	8 <sup>(c)</sup>
Ratio of liquor to wood.....	7.5	14.0	6.7	13.5	8.16	9.6	10.0	5.0
Per cent Na <sub>2</sub> O based on weight of wood.....	24.0	28.0	27.9	35.0	19.8	16.5	18.1	18.5
Strength of alkaline liquor, per cent Na <sub>2</sub> O.....	3.2	2.0	4.17	2.6	2.42	1.72	1.8	3.7
Causticity of alkali, per cent Na <sub>2</sub> O as NaOH in total Na <sub>2</sub> O as NaOH + Na <sub>2</sub> CO <sub>3</sub> .....			94.3	94.8	81.0	94.5	96.0	94.5
Time at 100 lbs. pressure, hours.....	2.25	4.0	3.5	3.25	2.75	2.5	2.75	3.0
TURPENTINE RECOVERED, gallons per cord.....	2.0	0.0	0.3	0.0	0.0	0.0	2.9	32.6
YIELD OF PULP ON DRY BASIS	{ per cent of resinous wood.....							
	{ per cent of "actual wood".....							
	..	22.5	22.3	22.8	25.2	25.9	27.0	24.0
		41.5	41.0	41.8	46.4	47.7	49.7	44.2

(<sup>a</sup>) Black liquor from preliminary extraction used as cooking solution.

(<sup>b</sup>) Soda cook on smaller chips. (<sup>c</sup>) Direct soda cook of resinous chips.

The over-all yield of approximately 25 per cent of pulp illustrates the practical drawback in treating this resinous material directly for pulp alone, not to mention the high consumption of alkali which would be involved in dissolving the rosin and the mechanical difficulties in cooking and washing. The true pulp yields are well within the range of ordinary practice. The figures between 45 and 50 per cent must be considered as most typical, inasmuch as the raw material is especially adapted to the production of somewhat raw, strong fiber for making high-grade wrapping papers, etc.

#### NATURE OF PRODUCTS

**TURPENTINE**—The crude turpentine obtained during alkali extraction represents the volatile oils of the wood practically unchanged by distillation from dilute alkali at low steam pressures. In the refining of the "crude turps" from the "Steam Distillation" process, it is customary to redistil after the addition of dilute alkali. It may be said, then, that the volatile oils from this alkali extraction process have already undergone the first steps in refining.

The direct product was in every case clear and only faintly yellowish in color. The oil was without the objectionable odor of "Destructive Distillation" tur-

pentine. The odor was pleasant and of an "essential oil" character, rather than of pure turpentine. This may be ascribed to the pine oil content.

It was not considered necessary to give particular attention to the refining of the crude turpentine. The methods have been carefully worked out and there are no special difficulties involved.

**ROSIN SOAP**—The proposed scheme provides for the recovery of rosin from the direct extract and first wash liquor by salting out the rosin soap with caustic soda. It has been shown that 75–85 per cent of the rosin can be obtained in this way from rich wood. The soap precipitates were soft, and more or less contaminated with material derived from the wood itself. Purification from the humus was accomplished by reprecipitation with caustic soda. It would seem logical to use the soap as such, without acidifying to liberate free rosin.

Ordinary papers are sized with rosin, added in the form of soap solution and finally precipitated by alum. By dissolving the soap precipitates obtained in the process under discussion, and heating with a certain amount of free rosin, it should not be difficult to provide an emulsion of the composition demanded by the paper maker.

There are possible drawbacks in a scheme of this kind. The presence of oils in size sometimes results in spotting of the finished paper. However, by careful

distillation of the crude turpentine during extraction of the wood, it is doubtful if more than a trace of oily matter would find its way into the finished size. The humus carried down by the colloidal sodium resinate detracts somewhat from the white color of the rosin soap and gives a brownish color to the solutions. It is a question whether the small proportion of humus in the original rosin soap would appreciably affect the value of the directly prepared size, except for use on white papers. Humic salts have even been suggested as possible sizing agents in themselves.<sup>1</sup>

**PAPER PULP**—In addition to the products mentioned above, it has been shown that the normal yield of high-grade pulp can be obtained from resinous pine by the methods described. The whole process, in fact, has been designed with this end in view. The two-stage treatment adapts itself to the employment of any of the so-called "alkaline" processes for the final production of fiber. It would not be desirable to use "sulfate" liquor for extraction of the rosin, but in a sulfate mill, where the two-stage treatment of rich wood was carried on in conjunction with ordinary pulping operations on lean wood, there should be no

<sup>1</sup> E. Rimman, *Swensk Kemisk Tidsskrift*, see *J. Soc. Chem. Ind.* Feb. 29, 1912, p. 183.



difficulty in providing for the extraction of the rich wood with caustic soda alone.

The pulp obtained from long-leaf pine is characterized by unusual length of fiber, the length being 4-6 millimeters, or about twice that of spruce fiber. This quality, coupled with the favorable strength and flexibility of the fiber, imparts to the finished paper unusual toughness and resistance to folding and bursting. It is well suited for making high-grade wrapping paper, board stock, etc. With further study of the methods for cooking, beating and bleaching, it is expected that the uses of the pulp will be greatly extended.

#### SIGNIFICANCE OF RESULTS

The data obtained in these investigations are not necessarily representative of those which would hold in industrial practice, nevertheless the results of the investigation clearly indicates the feasibility of a simple two-stage alkaline treatment for southern pine by which it is possible to obtain a high recovery of valuable products from the primary constituents of the wood. The crude products are isolated in a favorable state of purity and require little subsequent refining. The process is characterized by simplicity in manipulation and in separation of end products. Moreover, the materials used in the reduction, as well as the ultimate products themselves, are few in number and simple in nature.

There is no waste of alkali at any point. The portion withdrawn from the cycle in the form of precipitated sodium resinates serves to enhance the value of the rosin fraction. Incineration of the waste pulping liquor provides for the recovery of the balance of the alkali, within the practical limits of mechanical efficiency.

As mentioned before, practical application of this treatment of the more resinous materials could be carried out most conveniently as supplementary to ordinary pulp-mill operation on lean wood. Only slight modifications in certain of the existing digester units would be necessary to take care of the richer grades of pine. The supply of fat wood could be obtained by sorting the raw material received at the pulp mill or by procuring lightwood, etc., from independent sources.

There is also a possibility that the first stage of the process, namely, that of extraction with caustic soda or sodium carbonate, could be employed in treating those grades of resinous waste which would not lend themselves to final pulping. Charred or unsound wood might be steamed with dilute alkali for the recovery of rosin and turpentine, without provision for treatment of the extracted chips. The economic merits of such a scheme could be decided only by actual trial.

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#### THE DETERMINATION OF MINUTE AMOUNTS OF SULFUR DIOXIDE IN AIR<sup>1</sup>

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In the case of most of the determinations of small amounts of sulfur dioxide in air, which have so far

been made, considerable volumes of sample were available. Methods based upon the aspiration of a large amount of air through a small quantity of liquid, and the gravimetric estimation of the retained sulfur could therefore be used. In such cases the results showed the average sulfur dioxide content for various periods of time. The problem at present in hand was the estimation of sulfur dioxide at any particular instant in the air of railway tunnels.<sup>1</sup>

The approximate dilutions which were to be determined were ascertained by liberating given amounts of the gas in a closed room and noting the odor. It was found in this way that 10 parts per million produced an effect similar to that often experienced while passing through a smoke-filled railway tunnel.

In order to collect what might be termed instantaneous samples, use was made of evacuated 2.5 liter bottles. These were provided with seals made of short glass tubes passing through the stoppers. On breaking the tip of the tube, the air entered within a few seconds, and therefore constituted a fairly representative sample of the atmosphere at the particular point at which the seal was broken. It therefore became necessary to determine in 2.5 liter samples of air, amounts of sulfur dioxide varying from about 0.0025 to 0.05 of a cubic centimeter.

The determination of fairly large amounts of sulfur dioxide by iodometric titration can, of course, be made with considerable accuracy. The application of this method to the determination of very small amounts of the gas appeared to be simply a question of ascertaining the peculiarities of the iodine reaction at great dilution, and selecting those conditions most favorable to constancy and accuracy of results. Experiments were made with dilutions of sulfur dioxide of the order of magnitude under consideration, namely, one to twenty parts per million. The titrations were made in the 2.5 liter white glass bottles, using *N*/1000 iodine and thiosulfate solutions. In those cases in which an excess of iodine was used and the end point approached with thiosulfate, great difficulty was experienced in judging when the last trace of the blue color of the starch disappeared. It was also found that even in the absence of sulfur dioxide, direct titrations with iodine and thiosulfate solutions gave quite different results, depending upon whether the end point was approached from the side of appearance or of disappearance of the blue color of the starch indicator. This point showed that no method of determination of very small amounts of sulfur dioxide involving a back titration would be practicable.

The results of the extended series of experiments showed that satisfactory determinations can best be made by adding 5 cc. of 0.1 per cent aqueous starch paste to the bottle containing the sample, and after rotating in such a manner that the interior walls are entirely moistened, titrating with *N*/1000 iodine solution to appearance of the blue color of the starch iodide. The end point obtained in this manner is quite sharp, one or two drops of the iodine being

<sup>1</sup> A detailed account of the analytical results obtained by the method here described will be given in a bulletin of the Hygienic Laboratory, U. S. Public Health Service.

sufficient to produce the final distinct blue color. Blank titrations made in exactly the same manner in a bottle containing air free from sulfur dioxide, required an average of 0.3 cc.  $N/1000$  iodine to yield an equivalent color change in the aqueous starch solution. This correction must therefore be applied to the titrations made upon samples containing sulfur dioxide. Since the reaction between iodine and sulfur dioxide is represented by the equation  $I_2 + SO_2 + 2H_2O = 2HI + H_2SO_4$  and 1 liter of  $SO_2$  at  $0^\circ$  and 760 mm. pressure weighs 2.862 grams then 1 cc.  $N/1000$  iodine should correspond to 0.000032 gram or 0.0112 cc.  $SO_2$  (at  $0^\circ$  and 760 mm.). In order to test the reaction at great dilutions the titrations of given mixtures of air and sulfur dioxide as shown in Table I were made.

TABLE I RESULTS OF DIRECT TITRATION OF MIXTURES OF SULFUR DIOXIDE AND AIR WITH STANDARD IODINE SOLUTIONS

Composition of mixture		Cc. standard iodine (cor.)	Calc. vol. $SO_2$ ( $0^\circ$ and 760 mm.)	Per cent of actual $SO_2$ found
Cc. Air	Cc. $SO_2$ ( $0^\circ$ and 760 mm.)			
3875	1.8	13.35 $N/100$	1.49	83
250	1.8	13.5 "	1.51	84
3875	0.9	6.55 "	0.73	81
250	0.9	6.8 "	0.76	84
3875	0.9	6.75 "	0.76	84
250	0.9	6.7 "	0.75	83
3875	0.36	2.65 "	0.30	83
250	0.36	2.85 "	0.32	89
3875	0.36	2.75 "	0.31	86
250	0.36	2.75 "	0.31	86
3875	0.09	6.95 $N/1000$	0.078	87
250	0.09	7.25 "	0.081	90
3875	0.09	6.85 "	0.077	86
250	0.09	7.0 "	0.078	87
2500	0.09	6.8 "	0.076	84
2500	0.09	7.5 "	0.084	93
2590	0.09	6.9 "	0.077	86
2500	0.09	7.1 "	0.080	88
2500	0.09	7.5 "	0.084	93
2500	0.09	7.25 "	0.081	90
2500	0.09	6.55 "	0.073	81
2500	0.018	1.15 "	0.013	72
2500	0.018	1.05 "	0.012	66
2500	0.018	1.15 "	0.013	72
2500	0.018	1.1 "	0.012	68
2500	0.018	1.1 "	0.012	68
2500	0.009	0.8 "	0.009	98
2500	0.009	0.6 "	0.007	75

The sulfur dioxide was measured by successively diluting a given volume of the pure gas with air and transferring definite amounts of the mixture to partially evacuated bottles of the capacity indicated in the table under "Cc. Air."

An examination of this table shows that in all cases low results are obtained. The average for concentrations of  $SO_2$  between 0.09 and 1.8 cc. is 86 per cent and for concentrations below 0.09 (except Det. No. 27) it is 70 per cent. There are two possible explanations for the low results. Either the reaction of the iodine with the sulfur dioxide may be incomplete at this dilution, or else partial oxidation of the sulfur dioxide occurs when it is diluted with air. Some evidence upon the latter of these assumptions is contained in the table. Thus it will be seen that in practically all of the duplicate titrations made in large and in small bottles, slightly lower results are obtained in the larger bottles, that is, in the more highly diluted mixtures.

Also the percentage of sulfur dioxide recovered is lowest in the case of the more dilute mixtures. It may therefore be concluded that some oxidation takes place simply upon allowing sulfur dioxide to diffuse in a large volume of air of ordinary dryness.

In regard to the incompleteness of the reaction, it was pointed out by Volhard<sup>1</sup> many years ago that in titrating aqueous sulfurous acid solution with standard  $N/10$  iodine, less sulfur dioxide is found when the titration is made with the iodine, that is, to appearance of the blue starch color, than when made in the reverse direction. At  $1/10$  normal concentrations the difference amounted to about 5 per cent of the sulfur dioxide present. Results for more concentrated solutions are given, but none for solutions more dilute than  $1/10$  normal.

In order to obtain data upon this point an experiment was made by us as follows: A standard solution of sulfur dioxide was prepared by dissolving an accurately measured volume of the gas in distilled water and diluting to a known volume. The first dilution contained 1.097 grams  $SO_2$  per 1000 cc. The second dilution contained 0.1097 gram  $SO_2$  per 1000 cc.

a. Titrations made with the first dilution and  $N/10$  iodine:

10.38 cc.  $N/10$  iodine required 35.05 cc.  $SO_2$  solution = 98.6 per cent  $SO_2$  found.

35.05 cc.  $SO_2$  solution required 9.96 cc.  $N/10$  iodine = 83.0 per cent  $SO_2$  found.

b. Titrations made with second dilution of  $SO_2$  solution and  $N/100$  iodine:

10.1 cc.  $N/100$  iodine required 32.3 cc.  $SO_2$  solution = 91.5 per cent  $SO_2$  found.

32.3 cc.  $SO_2$  solution required 9.54 cc.  $N/100$  iodine = 86.2 per cent  $SO_2$  found.

c. Titrations made with second dilution of  $SO_2$  solution and  $N/1000$  iodine:

50.0 cc.  $N/1000$  iodine required 15.75 cc.  $SO_2$  solution = 92.5 per cent  $SO_2$  found.

15.0 cc.  $SO_2$  solution required 43.6 cc.  $N/1000$  iodine = 83.7 per cent  $SO_2$  found.

Although these results are not perfectly consistent, they show that the titration to appearance of the blue color of the starch indicator gives the lower results, and the actual percentage recovered is approximately equal to that found by titrating the sulfur dioxide and air mixtures in the large 2500 cc. white glass bottles, as reported in Table I.

A more detailed study of this incomplete recovery of sulfur dioxide by iodine titration would be of considerable interest, but further experiments were not made by us, since it was evident that for the purpose of the present investigation of tunnel air, greater accuracy was not required.

From a consideration of the above experiments it is evident that a correction factor for incompleteness of the reaction at the great dilutions must be applied to the iodine titrations. The selection of this factor was based upon the results shown in Table I. Here it is seen that for concentrations between about 4 and 40 parts per million the recovered sulfur dioxide lies between 70 and 86 per cent. It was therefore con-

<sup>1</sup> J. Volhard, *Liebigs Annalen*, **242** (1887), 93

cluded that the factor 1.3 would bring the results sufficiently near 100 per cent for all practical purposes.

There is one other point which must be taken into consideration in connection with the determination of small amounts of sulfur dioxide, and that is the rate of loss due to oxidation, on standing. It was early noticed that the presence of moisture hastens this loss very materially. Even in the case of bottles dried as carefully as possible and with the exercise of reasonable precautions to exclude moisture, it was found that the sulfur dioxide began to disappear within a short time. Some experiments were therefore made for the purpose of ascertaining how soon the titrations of given samples must be made in order that loss due to oxidation may be avoided. A series of experiments was first made with carefully dried bottles. The results are shown in Table II.

TABLE II.—SHOWING RATE OF DISAPPEARANCE OF SULFUR DIOXIDE FROM DILUTE MIXTURES WITH AIR IN DRY 2500 CC. BOTTLES

Volume of contained SO <sub>2</sub> (at 0° and 760)	Time of standing Minutes	Found vol. SO <sub>2</sub> (at 0° and 760)		Per cent SO <sub>2</sub> recovered
		N/1000 iodine (cor.) Cc.	SO <sub>2</sub> (at 0° and 760) Cc.	
0.09	10.0	6.45	0.094	104
0.09	20.0	6.75	0.098	109
0.09	65.0	3.6	0.052	60
0.09	90.0	6.3	0.092	100
0.09	135.0	5.15	0.075	83
0.09	160.0	4.5	0.065	72
0.09	225.0	2.85	0.042	47
0.045	0.5	3.1	0.045	100
0.045	14.0	2.55	0.037	82
0.045	30.0	1.6	0.023	52
0.045	45.0	0.95	0.014	31
0.045	60.0	1.35	0.019	43
0.045	75.0	1.25	0.018	40
0.045	100.0	1.55	0.022	50
0.045	130.0	1.55	0.022	50

In the case of the dry bottles it would appear from the results that the disappearance is the more rapid, the more dilute the sulfur dioxide. This, however, cannot be definitely concluded since the experiments with the moist bottles indicate that the moisture factor plays a much more important part than the concentration. The difference in rate of loss as shown by the first series of seven determinations and the second series of eight determinations in Table II, may, in fact, be due to inappreciable differences in moisture content of the laboratory air with which the dilutions were made in the two cases, rather than to the 50 per cent difference in concentration of the sulfur dioxide itself.

In the experiments with moist bottles the irregularities were so great that no conclusion in regard to the rate of oxidation of the sulfur dioxide could be drawn. In some cases about half of the added gas had disappeared within a few minutes, and in others a loss of only about 30 per cent had occurred in half an hour. In practically all cases only a small fraction of the used sulfur dioxide was recovered after one hour. These irregularities were found even in spite of special efforts to maintain uniform conditions for the experiments. The results demonstrated the necessity of using dry bottles for collecting the samples. They also indicate that except on very dry days it is necessary to make the titration within less than half an hour after collecting the samples in order to avoid low re-

sults due to gradual oxidation of the sulfur dioxide.

In order to test further the direct iodine titration method for sulfur dioxide, several series of determinations were made upon samples of air from a room in which given volumes of pure sulfur dioxide were liberated. The room was 9 ft. X 10 ft. X 13 ft. = 1170 cubic feet capacity and contained a rather large window and door. The walls were of painted plaster. No attempt to seal the cracks around the window and door was made. A large electric fan was arranged to cause a rapid circulation of the air in the room. For each experiment the given volume of sulfur dioxide was liberated quickly and after a 2 to 6 minute period of stirring with the fan, the seals on the first series of eight evacuated dry bottles placed near together on a table, were broken practically simultaneously. A second series of six samples were taken after an additional 5 to 10 minutes' stirring. These samples were titrated as quickly as possible in all cases. The analytical results are given below in the order in which the titrations were made:

*Experiment I*—Volume of SO<sub>2</sub> liberated = 500 cc. or, on the basis of the volume of the room, 15 parts SO<sub>2</sub> per 1,000,000. *First series* of samples taken after 2 minutes' stirring, contained, respectively: 5.0, 7.9, 6.4, 4.1, 1.9, 5.5, 0.9, 5.5 parts SO<sub>2</sub> per 1,000,000. *Second series* of samples taken after 6 minutes' stirring contained, respectively: 7.6, 6.0, 5.5, 6.7, 4.1, 5.5 parts SO<sub>2</sub> per 1,000,000.

*Experiment II*—Volume of SO<sub>2</sub> liberated = 500 cc. or 15.0 parts per 1,000,000. *First series* of samples taken after 5 minutes' stirring contained, respectively: 10.0, 9.9, 7.0, 5.0, 9.6, 1.2, 6.1, 5.8 parts SO<sub>2</sub> per 1,000,000. *Second series* of samples taken after 10 minutes' stirring contained, respectively: 6.1, 6.1, 5.8, 4.1, 4.7, 5.8 parts SO<sub>2</sub> per 1,000,000.

*Experiment III*—Volume of SO<sub>2</sub> liberated = 500 cc. or 15.0 parts SO<sub>2</sub> per 1,000,000. There were also liberated 3300 cc. of CO<sub>2</sub> (= 100 parts per 1,000,000) generated by mixing aqueous Na<sub>2</sub>CO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> solutions. The weather outside was cloudy and moist. *First series* of samples taken after 5 minutes contained, respectively: 3.5, 2.3, 1.8, 6.4, 3.2, 2.6, 1.2, 1.2 parts SO<sub>2</sub> per 1,000,000. *Second series* of samples taken after 10 minutes contained, respectively: 4.6, 7.0, 2.3, 1.8, 3.8, 3.2 parts SO<sub>2</sub> per 1,000,000.

*Experiment IV*—Volume of SO<sub>2</sub> liberated = 213 cc. or 6.4 parts per 1,000,000. *First series* of samples taken after 3 minutes contained, respectively: 5.2, 2.3, 1.2, 1.2 parts SO<sub>2</sub> per 1,000,000. *Second series* of samples taken after 6 minutes contained, respectively: 3.2, 2.3 parts SO<sub>2</sub> per 1,000,000.

It will be noted that in all cases considerably less sulfur dioxide was recovered than liberated. There appears to be an initial loss amounting to about 30 to 50 per cent of the liberated gas. The variation between the individual samples of the second series in each case is less than for the first series, due probably to the more thorough mixing after the longer period of stirring. The variations between the several experiments are very significant. Thus in Experiment III, made on a cloudy, damp day and in which considerable water vapor was set free during the generation of the carbon dioxide, the recovered sulfur dioxide is appreciably lower than in the case of Experiments I and II. The moisture content of the air, therefore, influences the loss of sulfur dioxide set free in the room to a very considerable extent.



## SUMMARY

It has been shown that very minute amounts of sulfur dioxide in  $2\frac{1}{2}$  liter samples of air can be determined by direct titration with  $N/1000$  iodine. A correction factor of 1.3 for the apparent incompleteness of the reaction at the great dilution must be applied. On account of the gradual oxidation of the sulfur dioxide, the titrations must be made within a short time after the collection of the sample. The presence of moisture hastens the loss by oxidation very materially.

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## THE ANALYSIS OF MAPLE PRODUCTS, IV

## The Composition of Maple Sugar Sand

By J. F. SNELL AND A. G. LOCHHEAD

Received January 7, 1914

**INTRODUCTION**—When, in July, 1911, Professor W. H. Warren's article "Sugar Sand from Maple Sap; A Source of Malic Acid,"<sup>1</sup> appeared, Mr. Lochhead had been engaged for some weeks in analyzing sugar sand and attempting to prepare malic acid from it. In carrying out my suggestion to treat the sand with dilute nitric acid, precipitate the malic acid as lead malate and liberate it by treatment with hydrogen sulfide, he had found that calcium bimalate could be crystallized out from the nitric acid solution, and transformed into free acid by treatment with oxalic acid—essentially the process recommended by Warren. Mr. Lochhead's work was presented to the Faculty of McGill University in 1912 as a thesis for the degree of M.Sc., but has not appeared in print. The present article prepared during Mr. Lochhead's absence is based upon his results. [J. F. SNELL]

## PREVIOUSLY PUBLISHED ANALYSES OF SUGAR SAND

When the sap of the sugar maple has been concentrated to a thin syrup by boiling, a precipitate is deposited, which is known to the sugarmaker as "sugar sand" or "niter." Two analyses of this precipitate,<sup>2</sup> published previous to Warren's paper, indicated a content of 33.75 and 40.10 per cent of calcium malate, respectively. These analyses included about 40 per cent of sugars and obviously referred to the crude unwashed materials. Warren<sup>3</sup> made a more detailed analysis of a single sample of washed sugar sand, which showed a calcium malate content of 68.64 per cent and a silica content of 7.74 per cent.

## DESCRIPTION OF SAMPLES

We have analyzed six washed samples, all of Quebec origin, five being the product of single sugar bushes, the other (No. 5) a mixture. The sources of the samples and the descriptions of the unwashed material are given in Table I. The samples were washed by mixing thoroughly with hot water and filtering with a Buchner filter, the process being repeated until the sweet taste disappeared. In most instances four

TABLE I—DESCRIPTION OF SAMPLES OF SUGAR SAND WASHED AND ANALYZED

No.	County	Description	Remarks
1	Argenteuil	Light brown	High land, shallow, gravelly soil, limestone bottom
2	Shefford	Light brown	High gravelly soil
3	Shefford	Darker than 1 or 2	High land, slate and loam
4	Shefford	Dark brown containing much syrup	
5	Shefford	Light colored	Mixture from different parts of Shefford Co.
6	Brome	Very dark, containing so much syrup as to make it somewhat fluid	

washings were sufficient. The washings invariably contained calcium as well as sugar. They readily underwent fermentation, liberating carbon dioxide and becoming acid in reaction.

The washed sugar sand was almost white and was non-hygroscopic. It had a specific gravity varying from 1.76 to 1.83 and averaging 1.80.

The loss of dry matter during washing was determined in Samples 1 and 5. In four experiments

TABLE II—RESULTS OF ANALYSIS OF WASHED SUGAR SAND

Sample	1	2	3	4	5	6	Average
H <sub>2</sub> O.....	0.21	0.69	0.69	0.57	0.17	0.11	
CaO.....	25.74	22.63	24.27	24.07	25.33	23.06	
MnO.....	1.87	1.38	1.80	1.63	1.49	..	
MgO.....	..	..	0.27	0.84	0.45	0.88	
CaH <sub>2</sub> O(a).....	53.73	46.49	47.14	44.32	50.73	44.88	
SiO <sub>2</sub> .....	6.16	18.55	13.74	15.03	10.65	13.82	
P <sub>2</sub> O <sub>5</sub> .....	..	0.99	0.70	0.82	0.33	0.29	
Total.....	87.71	90.73	88.61	87.28	89.15	83.04	
Ca.....	17.76	15.62	16.75	16.61	17.44	15.91	16.68
C <sub>2</sub> H <sub>2</sub> O <sub>4</sub> (b).....	61.17	52.90	53.64	50.44	57.73	51.06	54.49
Ratio 1:.....	3.44	3.38	3.20	3.04	3.31	3.21	3.26
CaC <sub>2</sub> H <sub>2</sub> O <sub>4</sub> calculated:							
(1) from Ca.....	76.22	67.03	71.88	71.28	74.83	68.28	71.59
(2) from C <sub>2</sub> H <sub>2</sub> O <sub>4</sub> .....	79.67	68.91	69.87	65.73	75.25	66.56	70.98
(a) Malic acid anhydride. (b) Malate radical.							

on No. 1 it varied from 51 to 55 per cent and averaged 52.7 per cent. In four experiments on No. 5 it varied from 49.5 to 53 and averaged 52.1 per cent.

## METHODS OF ANALYSIS

**Moisture** was determined by drying 10 grams at 100°. The *mineral constituents* were determined in the air-dry ash and calculated over to percentage of the original material. A trace of iron was found in all the samples.

**Malic acid** was determined by a method similar to and suggested by that of Warren, whose work had been published before our malic acid determinations were undertaken: 1 gram sugar sand and 25 cc. normal oxalic acid were heated on the water bath for an hour and a half. The product was filtered and washed, and the filtrate made up to 250 cc. Total acidity was determined in one 50 cc. aliquot. In another, the residual oxalic acid was determined by neutralizing with ammonia, acidifying with acetic acid, precipitating with calcium chloride, dissolving the washed precipitate in sulfuric acid and titrating with standard permanganate. The difference between total acid and residual oxalic acid represents the liberated malic acid.

<sup>1</sup> Warren, *Jour. Amer. Chem. Soc.*, **33** (1911), 1205.

<sup>2</sup> Bryan, U. S. Dept. Agriculture, Bureau of Chemistry, *Bull.* **134** (1910), 55. One of the analyses is original, the other is quoted from Indiana Agr. Expt. Station, 12th Annual Report, 1899, p. 74. The latter is also quoted and commented upon by Sy, *Jour. Franklin Inst.*, **1908**.

<sup>3</sup> Loc. cit.

## RESULTS

The results of our analyses are given in Table II. For comparison with Warren's analysis we give calcium (Ca) and malate radicle ( $C_4H_4O_6$ ), as well as lime and malic anhydride.

An unsatisfactory feature of the analyses is the large percentage of undetermined matter. This appears also in Warren's analysis, in spite of his determinations of sugar, ether extract, carbon dioxide and extraneous organic matter.

Evidently constituents of some little quantitative importance are unreached both by his methods of analysis and by ours. The Indiana analysis, likewise, shows about 10 per cent of undetermined matter. It is remarkable that Bryan's analysis shows only 1.66 per cent of "insoluble matter"—apparently including silica—and totals 98.23 per cent (assuming "malic acid" to mean malate radicle).

In two of our samples the calcium content is higher than in Warren's; in four it is lower. The average for all seven samples is 16.75 per cent. In malic acid four of our samples are higher and two lower than Warren's. The average for all seven is 54.06 per cent expressed as malate radicle. The ratio of malate to calcium for our samples is given in Table II. It is in three cases higher, and in three lower than the theoretical ratio for normal calcium malate, *viz.*, 3.29. The average for our six samples is 3.26. In Warren's analysis, this ratio is a little lower than the lowest of ours, *viz.*, 3.40 as against 3.04. The average for all seven samples is 3.22. These results would indicate that the calcium and malic acid, the chief constituents of sugar sand, are present almost wholly in the form of normal calcium malate, this salt constituting about 70 per cent of the washed material.

Silica is the only other constituent of sugar sand of any prominence. Its quantity varies in the seven samples from a little over 6 to a little over 18.5 per cent.

The quantity of phosphoric acid present is always small. It is interesting to note in this connection that in 1887 B. J. Harrington<sup>1</sup> in boiling down the sap of the ash-leaved maple (*Negundo aceroides* or *Acer negundo*) obtained a deposit containing no less than 64.91 per cent of *tricalcium phosphate*. He also found a large proportion of calcium phosphate in a similar deposit from the sap of *Acer rubrum* and based upon these results an opinion on that "if the nitre from the sap of *Acer saccharum*<sup>2</sup> were examined for phosphoric acid, it would here also be found to be a prominent constituent."

## SUMMARY

1. The analyses of six Quebec samples of washed, air-dried maple sugar sand are reported.

2. This material contains from 65 to 80 per cent of normal calcium malate, from 6 to 18.5 per cent of silica, minor quantities of manganese, magnesium and phosphorus, traces of iron and from 10 to 17 per cent of undetermined material.

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<sup>1</sup> Harrington, *Trans. Roy. Soc. Can.*, 6, Sec. 3, p. 39 (1887).

<sup>2</sup> Evidently referring to the hard or sugar maple, now designated *Acer saccharum*.

## MANUFACTURE OF UNFERMENTED GRAPE JUICE IN CALIFORNIA

By W. V. CRUICK AND C. J. HINTZE  
Received December 1, 1913

The present output of unfermented grape juice in California is estimated at 80,000 to 100,000 gallons yearly. Considering the size of the Viticulture industry in the state, this amount is very small in comparison with the production in the Eastern states. On the other hand, the possibilities are almost unlimited because California produces 55-60 million gallons of wine and a great quantity of table and raisin grapes. With the growth of the temperance movement, the popularity of grape juice will undoubtedly increase. California will be the logical source of supply because of its adaptability to the production of large quantities of grapes of high quality.

The varieties of grapes to be selected may either be the American varieties, which produce a juice with the well known "foxy" flavor, and which would satisfy the demand already created by such juices now on the market; or, as is the general rule in California, the European varieties of high flavor, such as are grown in the state at the present time, may be utilized. Among the former, California produces the Isabella and Concord, chiefly. Of the European varieties, the Muscat of Alexandria, Semillon, and Franken Riesling are suitable highly flavored white grapes, while the Cabernet is a suitable black grape of pronounced flavor. Besides high flavor, high acid is necessary. For white juice, Muscat may be taken to give flavor and blended with Burger or West's White Prolific which are high in acid but lacking in distinctive flavor. Both color and acid, as well as high flavor, are needed in red juice. For flavor Isabella grapes may be used; the acid and color may be obtained by mixing with them slightly underripe Alicante Bouschet or Alicante Ganzin juice, or by heating Zinfandel or other common black juice on the skins to 180° F. for a short time to extract the color.

The acidity of the juice in any case should be between 0.8 and 1.1 per cent as tartaric acid. The total solids (Brix or Balling) should be not higher than 20 per cent. The desired composition can usually be obtained by judicious blending. It may be said that one of the chief defects of a great deal of the juice at present is that due to the use of grapes too high in sugar and defective in acid.

The objects in the manufacture of grape juice are the attainment of high and agreeable flavor and perfect and permanent brightness in bottle. An outline of present commercial methods is given below and is followed by a summary of experimental results.

## OUTLINE OF PRESENT METHODS

The grapes are picked without any special regard to the proper degree of ripeness for grape juice making, usually at about 22 per cent Balling or more and crushed as soon as possible to prevent mold growth. The juice is drained from the crushed grapes and the pomace is pressed in a hydraulic press.

The free run and press juice are mixed and pasteurized at once at a temperature of 185° F. into 50 gallon

sterile barrels. Two forms of pasteurizers are in use, one type continuous and the other discontinuous. The former may be the familiar steam-jacketed copper or aluminum cookers used in canneries or may be a tank fitted with a steam coil. In either of these the juice must be kept in constant motion to prevent local overheating, which results in a cooked taste. The continuous pasteurizers have a steam-jacketed, tin-lined pipe through which the juice is passed. By varying the rate of flow of juice and the steam pressure, any desired temperature may be given the juice passing through it. The continuous pasteurizers require less labor and are in general more satisfactory than the discontinuous types.

If the acidity is too low, tartaric acid is added at the time of pasteurization. This is added by taste and not according to a chemical test of the acid.

The pasteurized juice is stored in barrels at least six months to allow the separation and settling of albumen coagulated by the heating and the separation of cream of tartar in the form of crystals. During this storage about 2 per cent of the juice ferments, due to action of yeasts that gain entrance through leaky barrels. This fermented juice may be used for wine or vinegar.

After this long storage the juice is racked from the sediment and brightened by simple filtration, if possible, or by one of the methods of clarification given below, followed by filtration.

By one method of clarification casein is added to the juice in sodium carbonate or ammonia solution. The acidity of the juice precipitates the casein which will, on settling out, carry down all suspended matter with it. The juice is filtered immediately after adding the casein, the whole process being carried out on the cold juice. It is bottled immediately and pasteurized in the bottle. By a second method of clarification egg albumen is added to the freshly racked juice in water solution and the mixture heated to 180° F. The heat coagulates the albumen, forming a fine network throughout the liquid, which, on settling, carries down all finely divided suspended matter with it. After this pasteurization the juice is stored in barrels several weeks. It is then filtered through some form of pulp filter and bottled. The bottles are closed with corks, Crown caps or Goldy caps. The Crown cap is the one so commonly used on beer bottles, soda water bottles, etc. The Goldy cap consists of an inner layer of cork that fits over the top of the bottle; over the cork is an enameled metal disc and over the disc is an aluminum cover that can be removed easily without the aid of an opener of any sort.

The bottled juice is pasteurized in an autoclave under slight pressure or in an open cooker at atmospheric pressure. The latter type is the one in more common use. It consists of a wooden tank with a false bottom. The bottles are placed on the false bottom and water is run into the pasteurizer to about three-fourths the height of the bottles. The apparatus is covered and the temperature brought to the desired point by a steam coil placed beneath the false bottom. It is essential that every part of the bottle be heated in

order that no mold spores may escape. Failure to observe this point is the cause of a great deal of moldy juice. A temperature is employed which is 5° F. below that of the previous pasteurization. If the temperature exceeds that of the preceding cooking, cloudiness is apt to develop, probably due to the precipitation of albumens not coagulated by the previous heating.

The pasteurized juice is stored a few weeks at the plant to ascertain if the treatment has been satisfactory. Cloudiness may develop, due to overheating, separation of cream of tartar or to mold growth, hence the need of making certain that the juice will remain clear after leaving the factory.

#### RESULTS OF EXPERIMENTS AND PROPOSED MODIFICATIONS IN PRESENT METHODS

Tests were made in 1912 and 1913 to ascertain if the juice could be clarified immediately after pressing from the grapes, or at least very shortly after pressing. If such a method could be developed it would save one heating at least, and would therefore lessen the cooked taste. Experiments in the laboratory on clarification of the muddy juice from the press and crusher gave negative results. Samples of the fresh juice were also filtered to give a bright juice, but on pasteurization these samples invariably became cloudy.

However, it was found that if the juice were allowed to stand 24 to 48 hours to deposit all suspended matter, it could be clarified without any great difficulty. This settling process is ordinarily termed defecation. During defecation, fermentation must be prevented. This may be done either by cold or sulfurous acid; preferably by aid of the latter. Pasteurizing the juice to prevent fermentation temporarily does not serve the purpose because heated juice will not defecate satisfactorily or completely. The sulfurous acid was used in all tests at the rate of 4 to 6 ounces per ton of crushed grapes. It was added in the form of potassium metabisulfite,  $K_2S_2O_5$ , which contains about 50 to 56 per cent  $SO_2$ . Twelve ounces of the metabisulfite per ton is equivalent to about 185 milligrams of  $SO_2$  per kilogram of grapes. Tests have shown that at least half of this disappears during subsequent treatment, so that the amount left in the final juice is far below the legal limit of 350 milligrams per kilo. After a few days it is practically all in the combined form, so that very little of the free or active form can be detected in the finished juice. The sulfurous acid tends to minimize the development of the cooked taste, which seems to be an oxidation phenomenon.

A number of substances were tried as clarifying materials, among them being casein, lactocoll (soluble casein), tannin and gelatin, egg albumen, tannin alone, tannin and isinglass and water glass alone. All tests were made by adding the fining materials to the freshly defecated juice, mixing them thoroughly with the juice and then heating to 185° F. The casein and lactocoll are precipitated by the acid of the juice; the gelatin by the tannin; the isinglass is precipitated by the tannin; the egg albumen is coagulated by the heating; and the water glass is broken up by the acidity of the juice to give  $SiO_2$  in hydrated form. All of the



precipitates are flocculent and on settling out tend to carry down all suspended material with them. This suspended material consists of small particles of pulp and grape proteins coagulated by the heating.

Casein, egg albumen and the isinglass-tannin finings gave the best results. Casein seems to be the most satisfactory material of the whole series tested because it gives a heavy precipitate that settles rapidly and completely and when used in moderate amounts gives a larger percentage of successful finings than any of the other materials.

The variety and composition of the juice has considerable influence on the clarification. Casein added at the rate of 5 ounces per 100 gallons of juice to Alicante Bouschet, Alicante Ganzin, Isabella, Zinfandel, Burger and Chasselas juices gave excellent results, the juices becoming perfectly bright in 24 to 48 hours after fining. Muscat juice treated in the same manner did not clear satisfactorily and had to be filtered after the fining process to render it bright. Ripe Muscat juice was very much more difficult to clear than slightly underripe juice.

Besides the above laboratory fining experiments, practical tests were made on several lots of juice at the plant of J. Swett and Son, Martinez, Calif. Five ounces of casein were added to each 100 gallons of Alicante Bouschet juice and the must was heated in an open cooker to 185° F. In 24 hours the juice had settled bright and remained bright in bottle after bottling and repasteurizing. Chasselas treated similarly gave similar results. Muscat treated in the same way did not clear well, but did give good results with egg albumen finings.

Both laboratory and winery tests demonstrated that grape juice clarified by casein or egg albumen and heating, when filtered 48 hours after fining, remained bright in bottle. The only objection found to this method of treatment was that cream of tartar separated out after the juice had stood a few days. This settles to the bottom of the bottle in the form of a layer of small crystals and detracts considerably from the appearance of the product. To white juice previously clarified and filtered, was added varying amounts of tartaric and citric acids. One set was kept at 22° C. and the other at 0-4° C. The addition of 0.2 per cent or more of tartaric acid caused an immediate separation of cream of tartar. The addition of as small an amount as 0.1 per cent tartaric acid caused a great increase in the rate of separation of cream of tartar at the lower temperature but seemed to have little or no effect at the higher temperature. There was no perceptible difference in the rate of separation of cream of tartar at the two temperatures in the untreated samples. This indicates that to get the greatest effect of cooling on the separation of cream of tartar from grape juice a small amount of tartaric acid should be added before cooling. The citric acid in small amounts, *i. e.*, 0.05 and 0.1 per cent, prevented the separation of cream of tartar but at 0.3 per cent seemed to slightly hasten the separation of the cream of tartar.

The effect of the tartaric acid is no doubt due to

the increase of tartrate ions. This would cause a repression of the ionization of the cream of tartar and because of the slight solubility of the undissociated form causes it to separate from solution.

In view of these tests it is recommended that the process of grape juice manufacture be modified to conform to the following outline:

1. Use a mixture of ripe grapes to give flavor with grapes of high acid to remedy the lack of acid in the ripe grapes.

2. Add 8-12 ounces of potassium metabisulfite<sup>1</sup> per ton of grapes at the crusher, to prevent fermentation during defecation.

3. Allow the juice to defecate 24-48 hours and rack from the sediment.

4. Add to each 100 gallons of juice 4-6 ounces of casein dissolved in sodium carbonate or ammonium hydroxide.

5. Add a small amount of tartaric acid to increase the rate of separation of the cream of tartar.

6. Heat the juice to 165° F. and store in 50 gallon barrels until most of the excess cream of tartar has separated.

7. Rack from the sediment and filter, if necessary.

8. Add a small amount of citric acid to prevent further separation of cream of tartar, and bottle.

9. Pasteurize in bottle at 160° F.

Note that a temperature of 165° F. is recommended for the first cooking and 160° F. for the final heating. These are high enough temperatures to keep well handled juice and will give a great deal less of the objectionable cooked flavor so evident in all grape juice now on the market.

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## THE COMPARATIVE VALUES OF SOME ESSENTIAL OILS AS PRESERVATIVES OF CANE SUGAR SOLUTIONS

By C. B. COCHRAN<sup>2</sup> AND J. H. PERKINS<sup>3</sup>

Received October 17, 1913

**THE FERMENTATION TEST USED**—A measured amount of Fleischmann's yeast was thoroughly mixed with a measured amount of syrup. Portions of the syrup were then put in two fermentation tubes and kept in an incubator at a constant temperature. The percentage of gas was noted once each day. Where only one percentage is stated in the following tables, the duplicate tube contained the same amount of gas. The amounts of yeast and syrup and the temperature are stated in each table.

**THE OILS USED**—The essential oils, purchased from the most reputable firms, were analyzed by us and found to be pure.

**THE SYRUPS USED**—Unless otherwise stated, the

<sup>1</sup> It should be remembered that this treatment will produce a juice illegal in several states where the pure food laws do not allow the use of sulfurous acid as a preservative, although the amounts used cannot be said to act as preservative because fermentation will take place in such juice after standing a few days. The total amount left in the juice will be less than 1/5 the U. S. maximum of 350 mg. per kilogram.—[EDITORS]

<sup>2</sup> Chemist for Dairy and Food Department of Pennsylvania.

<sup>3</sup> Chief Chemist for The Charles E. Hires Company.



## CONCLUSIONS

1—Oils are named in the following in the order of their value as preservatives:

Fresh syrups: 0.011 per cent sassafras apparently equal to 0.011 per cent star-anise; 0.011 per cent cassia; 0.22 per cent ginger.

Five-week old syrups: 0.11 per cent lemon; 0.11 per cent star-anise; 0.11 per cent sassafras; 0.001 per cent orange.

Six-week old syrups: 0.22 per cent lemon; 0.022 orange.

Six and one-half-month old syrups: 0.022 per cent cassia; 0.22 per cent sassafras (apparently equal to 0.045 per cent star-anise); 0.22 per cent lemon.

2—Ginger is a poor preservative. Syrups containing this oil fermented a few months after they were made.

TABLE V—SASSAFRAS, STAR-ANISE, LEMON AND ORANGE COMPARED

Specific Gravity of Syrups, 1.2563 at 20° C.

One Thirty-second of a Fleischmann's Yeast Cake in 1 Fluid Oz. Syrup

Temperature of Incubator, 30–31° C.

Per cent of oil	Series 5 Fresh syrup		Series 5a 8 mos. old	Sp. gr. 8 mos. old
	Per cent gas	in days	Per cent gas	Per cent gas
0.011 sassafras	10 & 2	7		
0.011 sassafras	20 & 100	11		
0.022 sassafras			None in 10 days	1.259
0.0083 sassafras	10	7		
0.0083 sassafras	88 & 100	12		
0.0056 sassafras	20 & 23	4		
0.011 star-anise	2 & 5	7		
0.011 star-anise	25 & 100	11		
0.022 star-anise			None in 10 days	1.2568
0.0083 star-anise	10	7		
0.0083 star-anise	80 & 100	12		
0.0056 star-anise	32 & 40	4		
0.011 lemon	None	8		
0.011 lemon	0 & 43	12		
0.002 lemon			80 & 100 in 2 days	
0.0083 lemon	1/2	7		
0.0083 lemon	80 & 100	11		
0.0056 lemon	1/2 & 1	5		
0.0056 lemon	20 & 30	7		
0.011 orange	8 & 10	5		
0.011 orange	85 & 100	7		
0.0083 orange	55 & 60	4		

## CONCLUSIONS

1—That lemon as a preservative is superior to star-anise and sassafras so far as the withstanding of the above fermentation test on the freshly mixed syrups is concerned. (See conclusion No. 1, Table IV and, also, the following conclusion No. 4)

2—That there is little difference between the preservative powers of star-anise and sassafras, the latter, however, appearing to be a trifle the better.

3—That orange is inferior to star-anise, sassafras and lemon as a preservative.

4—Syrups containing lemon resist fermentation much more when just mixed than they do after they have been kept for some time. As pointed out before, this tendency of the old syrups containing oils to ferment may be due to an increase in the fermentability of the syrups brought about by inversion.

PHILADELPHIA

## THE COMPARATIVE VALUES OF SOME ESSENTIAL OILS AS PRESERVATIVES OF STARCH SYRUPS

By C. B. COCHRAN AND T. H. PERKINS

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THE FERMENTATION TEST USED—A measured amount of magic or Fleischmann's yeast was thoroughly mixed with a measured amount of syrup. Portions of the syrup were then put in two fermentation tubes and kept in an incubator at a constant temperature. The percentage of gas was noted once each day. Where only one percentage is stated in the following tables, the duplicate tube contained the same amount of gas. The kind and amounts of yeast and syrup and the temperature are stated in each table.

THE OILS USED—The essential oils, purchased from the most reputable firms, were analyzed by us and found to be pure.

THE SYRUPS USED—The oils were mixed with 95 per cent alcohol—one volume of oil to 9 of the alcohol. The oils in this form were then thoroughly mixed with the syrup in the proportions desired.

"Karo Corn Syrup" was used, all tests being made on syrups from the same can.

TABLE I—ANISE, CLOVE, CASSIA, WINTERGREEN, SASSAFRAS, SPEARMINT AND PENNYROYAL COMPARED

1/16 of a Fleischmann's Yeast Cake in 50 Cc. of Syrup

Temperature of Incubator, 32° C.

Specific Gravity of Syrup, 1.243 at 20° C.

Oil	Per cent of oil	Time Days	Result
			Per cent gas
Anise	0.026	7	80
Clove	0.026	1	100
Cassia	0.026	1	70
Wintergreen	0.026	1	100
Sassafras	0.026	6	100
Spearmint	0.026	2	100
Pennyroyal	0.133	7	None
None		1	100

CONCLUSIONS—The oils are here named in the order of their value as preservatives as determined by the above tests:

(1) Anise, (2) sassafras, (3) cassia, (4) spearmint, (5) wintergreen and (6) clove.

TABLE II—CLOVE, CASSIA, SASSAFRAS, JUNIPER BERRY, CITRONELLA, WINTERGREEN AND PEPPERMINT COMPARED

1/16 of Fleischmann's Yeast Cake in 50 Cc. of Syrup

Temperature of Incubator, 32° C.

Specific Gravity of Syrup, 1.248 at 20° C.

Oil	Per cent of oil	Time Days	Per cent gas
Clove	0.04	4	10
Juniper berry	0.08	4	100
Peppermint	0.08	9	None
Citronella	0.08	10	12
Cassia	0.04	5	100
Sassafras	0.04	9	15
Wintergreen	0.04	2	100
None		1	100

CONCLUSIONS—I—When 0.04 per cent is used, the value of the oils is as follows:

(1) Sassafras, (2) clove, (3) cassia, (4) wintergreen.

II—When 0.08 per cent is used, the value of the oils is as follows:

(1) Peppermint, (2) citronella, (3) juniper berry.

III—0.04 per cent of sassafras, or clove, or cassia is better preservative than 0.08 per cent of juniper berry.



TABLE III—LAVENDER, SWEET FENNEL, CARAWAY, CORIANDER, SWEET BIRCH AND SASSAFRAS COMPARED

$\frac{1}{15}$  of a Fleischmann's Yeast Cake in 50 Cc. of Syrup  
Specific Gravity of Syrup, 1.1925 at 20° C.  
Temperature of Incubator, 32° C.

Oil	Per cent oil	Time Days	Per cent gas
Lavender.....	0.2	1	100
Sweet fennel.....	0.2	7	30
Caraway.....	0.2	1	100
Coriander.....	0.2	7	None
Sweet birch.....	0.08	7	50
Sassafras.....	0.08	7	None

CONCLUSIONS—I—Coriander is superior to sweet fennel, which in turn is superior to lavender and caraway. The latter two oils have practically no value as preservatives when 0.2 per cent is used.

II—Sassafras is decidedly superior to sweet birch.

III—Sassafras in these tests is superior to any one of the above oils, with the possible exception of coriander.

TABLE IV—CLOVE, JUNIPER BERRY, PEPPERMINT, CASSIA, SASSAFRAS, WINTERGREEN, ANISE, AND SPEARMINT COMPARED

$\frac{1}{15}$  of a Magic Yeast Cake in 50 Cc. of Syrup  
Specific Gravity of Syrup, 1.248  
Temperature of Incubator, 32° C.

Oil	Per cent oil	Time Days	Per cent gas
None.....	..	1	100
Clove.....	0.04	2	100
Juniper berry.....	0.08	2	100
Peppermint.....	0.08	3	100
Cassia.....	0.04	4	100
Sassafras.....	0.04	4	100
Wintergreen.....	0.04	2	100
Anise.....	0.04	3	100
Spearmint.....	0.04	2	100

CONCLUSIONS—I—In these tests, 0.04 per cent of cassia seems to be equal to the same amount of sassafras, and superior to 0.04 per cent of anise, which in turn is superior to 0.04 per cent of spearmint or wintergreen.

II—It will be noted that these results differ somewhat from similar tests made with Fleischmann's yeast.

PHILADELPHIA

## ESTIMATION OF SUCROSE IN THE PRESENCE OF LACTOSE AND IN THE MILK PREPARATIONS<sup>1</sup>

By JITENDRA NATH RAKSHIT

Received December 21, 1913

The practical use and importance of the method of estimation of sucrose and lactose in their mixture, chiefly depend on the presence of the former in the sweetened condensed milks and other milk preparations. All the difficulty arises from the fact that the milk sugar also undergoes hydrolysis during the inversion of cane sugar by mineral acids. Stokes and Bodmer<sup>2</sup> described a method, the principle involved in which is the titration of a portion with Pavy's ammoniacal copper solution and that of another part after boiling with 2 per cent citric acid for ten minutes and then neutralizing. Boiling with citric acid was

<sup>1</sup> The estimation of sucrose in presence of lactose, with special reference to milk products, has also been thoroughly investigated by the Association of Official Agricultural Chemists. See Proceedings, 1906, pp. 98-101; 1907, pp. 53-9; 1908, pp. 152-9. In this connection should be mentioned the method of Bigelow and McElroy (*J. Am. Chem. Soc.*, **15**, 668), who determined sucrose in condensed milk by polarization before and after inversion with yeast or invertase. [Editors]

<sup>2</sup> *Analyst*, **10**, 62.

expected to invert the cane sugar without affecting the other. The difference in reducing power would account for the cane sugar. E. W. T. Jones,<sup>1</sup> in a modification of the above process of inversion, recommended that it should be kept in boiling water with 1.6 per cent citric acid for half an hour. F. Watts and H. A. Tempany<sup>2</sup> have shown that the inversion of cane sugar is fairly complete in ten minutes when only the two sugars are present, but is very greatly retarded in the presence of milk constituents. These authors have suggested that to obtain satisfactory results the boiling should be continued for forty minutes. In analyzing several samples of condensed milks it was observed that even boiling for that period was not always sufficient for complete inversion—the results obtained were too low. In addition to the inconvenience of the lengthy time of boiling the method does not yield reliable results in all cases in the presence of milk constituents.

The principle of the following method is simple, and works well for practical purposes. The percentage of lactose in the solution is first determined by titration with Fehling's solution, then a measured quantity of Fehling's solution is boiled with a calculated quantity of sugar solution so that all the copper may be thrown out of solution with the simultaneous consequent decomposition of all lactose when cane sugar alone will be left in solution, which can be readily estimated after the usual inversion and neutralization.

A solution was prepared containing 1 and 2.5 per cent of lactose and sucrose respectively. In titrating 10 cc. Fehling's solution, 6.9 cc. sugar solution (equivalent to 0.98 per cent lactose) were required. Twenty cc. Fehling's solution were placed in an Erlenmeyer flask, and 13.8 cc. sugar solution and 60 cc. water were added. The solution was heated to boiling for 5 minutes or until the reduced copper coagulated. It was then filtered hot through fine filter paper to another similar flask. The filtrate should be perfectly clear; no copper should remain either in solution or in suspension. Next, 10 cc. of strong hydrochloric acid were added and gently boiled for 10 minutes, cooled, neutralized with sodium carbonate and made up to 200 cc. Ten cc. Fehling's required 27.6 cc. of the above sugar solution, which is equivalent to 2.49 per cent sucrose in the original solution. Similarly the following estimations were made:

Percentage found		Percentage taken	
Sucrose	Lactose	Sucrose	Lactose
8.10	4.00	8.10	4.00
20.08	4.00	20.00	4.00
3.00	5.95	3.00	6.00
15.04	5.95	15.00	6.00

It is thus seen that the method is quite satisfactory in the case of mixtures of pure sugars.

In the examination of milks and milk preparations, they are usually coagulated first by cautious addition of dilute citric acid, adding drop by drop and shaking alternately. An excess of citric acid makes the subsequent filtration difficult, otherwise it is very easy and

<sup>1</sup> *Analyst*, **14**, 81.

<sup>2</sup> *Ibid.*, **30**, 119

rapid. The filtrate after neutralization is examined for sugars as before.

A sample of milk was taken which was found to contain 4.64 per cent milk sugar. Four flasks of 250 cc. capacity were filled with 100 grams of the above milk and 5, 10, 20 and 50 grams of pure cane sugar were added to them, respectively. Ten grams of each of the above prepared solutions were taken in 100 cc. flasks, and made up to 100 cc. From each, 50 cc. were taken, placed in four other 100 cc. flasks, and coagulated with 2 per cent citric acid solution added drop by drop, shaking all the while by a rotatory motion. These were filtered and the filtrates made up to 100 cc. and the sugars were estimated as before.

Percentage of lactose		Percentage of sucrose	
Found	Calculated	Found	Calculated
4.40	4.41	4.73	4.76
4.24	4.22	9.03	9.09
3.86	3.86	16.60	16.67
3.12	3.09	33.40	33.33

Some sweetened condensed milks were examined and the sugars estimated by the above method, starting with a 10 per cent solution. The following results were obtained:

Brand	Ash proteid fat lactose sucrose	Total solids by evapora- tion
1. Best skimmed condensed milk.....	70.7	70.2
2. Nestle's condensed milk, "Nest Brand".....	74.2	74.8
3. Milk-maid brand.....	70.8	70.1
4. Best skimmed condensed milk, cow and calf brand.....	75.1	75.6

In conclusion, I have much pleasure in expressing by best thanks to Mr. R. L. Jenks, Chemical Examiner for Customs and Excise, for his kindly allowing me to analyze several samples of condensed milks.

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### THE SOLUBILITY OF DEXTRIN<sup>1</sup>

By W. K. LEWIS

Received December 26, 1913

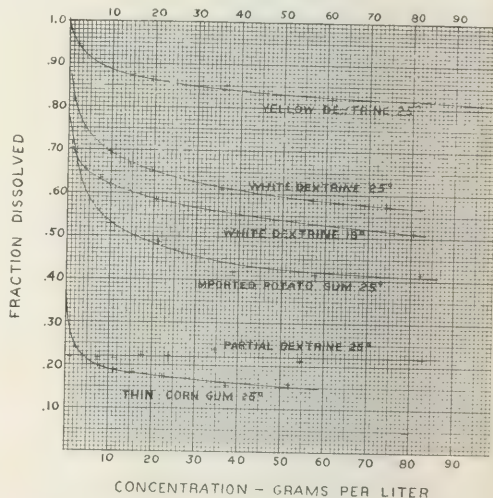
In an attempt to find a rapid method of determining the proportion of dextrin soluble in cold water, the author some time ago treated weighed dextrin samples with known amounts of water in the tubes of a centrifuge, and after thorough agitation separated the suspended insoluble matter by whizzing. The soluble portion was determined by the evaporation of an aliquot part of the clear solution. The ratio of water to sample was varied to insure sufficient solvent so that the solution should not be saturated with respect to any of the soluble constituents of the original dextrin. It was surprising to find that the soluble fraction increased rapidly with dilution.

If a physical mixture of a soluble and an insoluble substance be treated with increasing amounts of a solvent, we shall first obtain a saturated solution of the solute at the temperature employed, the excess solute remaining undissolved. During this stage the concentration of the solution obtained will remain

<sup>1</sup> All data quoted in this article are taken from a thesis by C. W. Hobson, submitted in partial fulfillment of the requirements for the S.B. degree at the Massachusetts Institute of Technology.

constant. After sufficient solvent has been added to dissolve the whole of the soluble substance, further addition will dilute the solution without increasing the amount dissolved. In the case of dextrin, however, no matter how small an amount of water be employed, under no condition does the concentration of the solution obtained remain constant, while on the other hand the addition of further solvent never fails to dissolve additional dextrin, although the use of no amount of water, however large, will dissolve the whole of the sample.

This unexpected behavior seemed worthy of quantitative study, and a large number of dextrans were examined in the following way: Weighed samples were introduced with known amounts of water into well stoppered bottles and shaken in a thermostat. After a certain time a part of the mixture was whizzed in a centrifuge, and the water-soluble matter determined by evaporation of an aliquot part of the solution. This was repeated until no further change in the concentration of the solution occurred, requiring at no time over twenty-four hours. Characteristic results are shown graphically by the following curves, the soluble frac-



tion of the dextrans being plotted as ordinates, abscissae being the concentration of the solutions obtained.

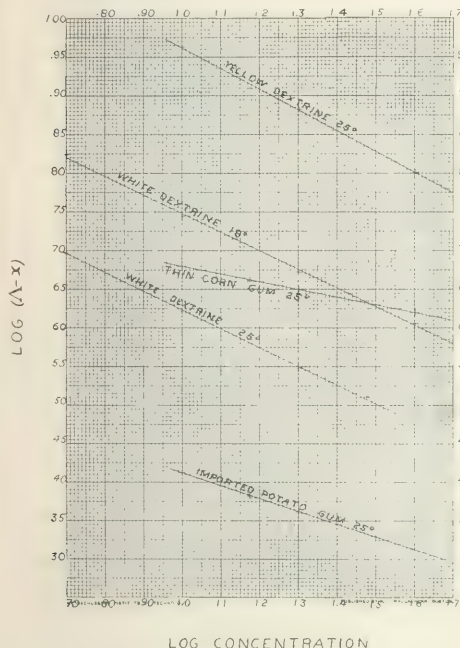
With the idea in mind that the insoluble portion of the dextrans might serve as a body on which the soluble portion could be adsorbed, these quantitative results were studied in the following way: Call the fraction of the dextrin insoluble in water, however great in amount, at the temperature in question,  $r - \Lambda$ . It follows that an indefinitely large amount of water will dissolve the fraction  $\Lambda$ . The fraction actually dissolved, as determined by experiment, is designated by  $x$ . The fraction soluble in water infinite in amount, but retained on the insoluble portion under the conditions in question, is  $\Lambda - x$ . The concentration of the solution, expressed in any suitable way, call  $c$ . If the

soluble portion unaffected by the water be adsorbed on the insoluble residue, one would expect the relationship to be represented by the adsorption equation, which in this case will be  $\Lambda - x = kc^{1/n}$ . Taking the logarithms of both sides:

$$\log (\Lambda - x) = \log k + 1/n \log c.$$

This requires that the logarithm of the soluble portion remaining undissolved under the conditions of the experiment shall be a straight line function of the logarithm of the concentration of the solution.

It is of course theoretically possible to determine the insoluble residue by treatment of the dextrin with an indefinitely large amount of water. This is,



however, difficult, and it is wiser to determine  $\Lambda$  in the following way: If there exist any value of  $\Lambda$  which will make the logarithm of  $\Lambda - x$  a straight line function of the logarithm of  $c$ , for all values of  $c$  however small, then this value of  $\Lambda$  is a most probable one for the soluble fraction of the dextrin. The data of the previous plot were tested by plotting  $\log (\Lambda - x)$  as ordinates against  $\log c$  as abscissae, different values of  $\Lambda$  being chosen. It was found that by varying the value of  $\Lambda$  the curve could be made concave either up or down, and that a suitable intermediate value of  $\Lambda$  would in all cases straighten out the plot. These plots are shown in the above diagram.

It is found from these results that at 25° C., the assumption of the presence in the dextrin of a residue insoluble in water, upon which a fraction of the soluble portion is adsorbed, offers a quantitative explanation of the behavior of the dextrin on treatment with water. It is desired to point out that not only this

insoluble fraction, but the two constants of the adsorption equation—namely,  $k$  and  $n$ —are highly characteristic of the dextrin employed, and in the opinion of the author offer a better means of distinguishing between samples of dextrans than any other method hitherto suggested. For the purpose of testing dextrans by this method, the procedure to be employed is to treat weighed samples of the dextrin with known amounts of water in a thermostat for approximately twenty-four hours, and determine the water soluble portion by evaporation of an aliquot sample of the liquid after whizzing in a centrifuge. The easiest method of determining the constants of the dextrin will then be to assume values for the total soluble fraction  $\Lambda$ , and to plot the logarithm of  $\Lambda - x$  against the experimental values of the logarithm of  $c$  until a chosen value of  $\Lambda$  results in a straight line. This value of  $\Lambda$  is the soluble portion, the slope of this line is  $1/n$ , and the intercept of this line is the logarithm of  $k$ . For the dextrans plotted, these constants are tabulated below:

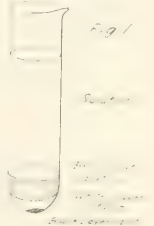
Substance	$\Lambda$	$1/n$	$k$
Yellow dextrin	25° 0.995	0.272	17.20
White dextrin	25° 0.935	0.250	7.48
White dextrin	18° 0.800	0.240	9.62
Imported potato gum	25° 0.920	0.168	3.81
Thin corn gum	25° 0.400	0.100	6.05

As shown in the first plots, one "Partial Dextrin" was found, the solubility of which is independent of the amount of water used, 22 per cent being dissolved in all cases. This sample is probably made by mixing a highly hydrolyzed product (practically a grape sugar) with untreated starch, adsorption being absent owing to the low molecular weight of the soluble portion.

It is not wished to have it understood that the author considers the results here presented as proof that adsorption is necessarily the explanation of the phenomena observed. Dextrans are unquestionably highly complex bodies, the components of which vary in solubility, and it is easily possible that the behavior on treatment with increasing amounts of water is due to the solution of increasingly insoluble components.<sup>1</sup> Such a hypothesis, however, it is impossible to express in mathematical form, whereas the suggestion which is here offered has shown itself in the cases so far tested capable of simple and exact algebraic treatment. Merely as a matter of empirical presentation of the results, therefore, it is considered that the proposed hypothesis justifies itself, and it is commended for use until further light is thrown upon the problem of the nature of the dextrans.

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<sup>1</sup> That something of this nature occurs is shown by the appearance of the deposit in the bottom of the tube after whizzing. This deposit consists of two distinct layers: the upper one is a jelly, readily soluble in warm water, and the lower one opalescent, lighter in color on that account, and less readily soluble. Beneath this is usually a slight amount of dirt. This appearance is indicated in Fig. 1.





## ANALYSES SHOWING THE COMPOSITION OF THE DIFFERENT GRADES OF COMMERCIAL PACK PEAS

By JOHN C. DUBOIS

Received November 19, 1913

Knowledge that the maturity of the pea is an important factor in its composition led to an investigation of the different grades of canned peas put out by an Indiana packing concern. Work on peas has been conducted chiefly by chemists who obtained their samples from the open market. The non-uniformity of methods used in grading and packing seriously interfered with any careful work in determining the exact effect of size and age upon the composition of the pea. Data at hand give information regarding the composition as to the size of the canned pea: none, however, are available showing changes in composition that may result with the maturing of the pea; A noticeable fact shown by the work of chemists is the utter unreliability of the label as a guide to the composition of the product. This work may, in a measure, assist in the establishment of standards of composition for each of the grades of canned peas.

The work of McElroy and Bigelow of some twenty years ago gives us<sup>1</sup> some analyses made of a large number of samples, of both American and foreign origin. No information is given as to system of grading as to maturity—if any system did exist. Dubois<sup>2</sup> in 1910 made the analyses of more than one hundred samples of canned peas. He draws conclusions regarding composition as to size but has no data for determining the effect of age upon composition. Street,<sup>3</sup> the same year, published results of one hundred and eleven samples but, without the history of the samples and method used in grading and sizing, based all tabulations on label statements.

Different systems of sizing and grading employed in various plants and the overlapping of one grade into the next tend to reduce the results of different grades to an average rather than differentiate between them. Since the samples were raised in different parts of the country, the matter of soil, rainfall and climate would be interfering factors.

Consequently, it was thought that if the common analytical factors were determined on the product put out by a single plant where uniform methods were used in sizing and grading, where the same variety of peas were packed, and one system used in packing and processing, there might prove to be a definite relation between the composition and the grade of the pea. While it has been shown<sup>2</sup> that the ratios existing between the organic plant constituents are different for different sizes of peas, no literature has been published showing the relations existing among the various inorganic plant factors for these samples. In view of this fact analyses were made showing the calcium, magnesium and phosphoric acid content of each grade of pea. A table has been calculated showing to some degree the composition of the ash of each grade.

In undertaking this work, eleven samples of canned peas were obtained: from a local packing concern, ten of these representing three brands and several grades of each brand and the eleventh being a sample of so-called "soaked peas."

## THE PACKING PROCESS

The peas used in this pack were grown in central Indiana within a radius of ten miles of the packing plant. The soil in this section is uniform, consequently that factor does not influence any particular grade. The season of packing usually extends from June 10th to July 15th.

The peas are mowed, loaded on wagons and hauled to the vining and thrashing machines. The hulled peas are passed through a squirrel cage washer into a grading tank of dilute brine (sp. gr. 1.07). The younger peas float in this solution and are removed by an elevator to a bin for subsequent grading as to size. This quality of pea is used for the Polk's Best Brand. The peas which have sunk to the bottom are carried by an elevator into a strong brine grading tank (sp. gr. 1.11). This brings about another grading, some floating and some going to the bottom. Those floating are made into the Greenwood Brand; those sinking, the harder and the more mature peas, into the May Day.

Each of these three classes of peas is made up of large and small sizes. It is desirable that the peas of a can be of uniform size. In factory practice each class is separated into five sizes. Beginning with the largest and going to the smallest, the names assigned to these five sizes are Marrow Fat, Early June, Sifted June, Extra Sifted June and Petit Pois. These trade names apply only to the size of the pea and have nothing to do with the season of packing. The grading is accomplished by means of perforated cylinders through which the peas pass.

After proper sizing the peas are blanched. The blancher is a continuous washer in which the peas are held in hot water for a certain period. In blanching two results are accomplished: (1) The outside mucous coat is removed from the pea and with it some of the green coloring matter so that the liquor of the can may be clear; (2) and to force water into the pea so that it may be tender. The time for blanching depends entirely upon the maturity of the pea. Blanching is not done "by rule of thumb" but by competent workmen who very carefully determine when the peas have taken up the right amount of water, when the right amount of color has been removed, etc. In general the time varies from two to five minutes.

From the blanchers the peas go to the filling machines. These put a certain weight of peas, varying according to size and quality into the can and add the liquor, a salt sugar solution (24 pounds of salt and 24 pounds of sugar to 500 gallons water) sufficient to fill the can. The lid is put on, sealed and the cans sent to the retorts for processing where they are heated at 240° Fahrenheit for 30 minutes.

## PHYSICAL EXAMINATION

The contents of each can were poured upon a sieve of  $1/8$  inch wire mesh and allowed to drain for one min-

<sup>1</sup> U. S. Department of Agriculture, Bureau of Chemistry, *Circ.* 54.

<sup>2</sup> U. S. Department of Agriculture, Bureau of Chemistry, *Bull.* 13.

<sup>3</sup> Conn. Agr. Exp. Station Report, 1910. U. S. Dept. of Agriculture, Bur. of Chemistry, *Bull.* 137.

ute. The greatest total weight (Table I) was 612 grams in the sample of "Soaked Peas." The maximum total of the fresh peas was 598 grams and the minimum 581 grams. The maximum weight of drained peas was 421 grams. This sample, 7247 B, undoubtedly had an excess of peas as would be indicated by the condition of the sample, "Peas all broken," "Liquor very turbid." The minimum of drained peas was 322 grams. This can had an excess of liquor. As a rule the small grades of peas were accompanied by the larger per cent of liquor.

TABLE I—PHYSICAL EXAMINATION OF CANNED PEAS

Label on can			Appearance of contents		Contents in grams		Peas and liquor			
							Drained		Gravity	
Sample	Brand	Grade	Peas	Liquor	Total	Drained	Drained	Drained	Peas	Liquor
7246 B	May Day	Marrow Fat	Peas all broken	Liquor very turbid	581	388.5	192.5	66.9	33.1	1.065
7247 B	May Day	Early June	Peas all broken	Liquor very turbid	594	421	173	70.9	29.1	1.123
7248 B	May Day	Sifted June	Slightly sprouted and broken	Turbid	590	322	268	54.6	45.4	1.106
7252 B	Greenwood	Early June	Large and broken	Somewhat turbid	598	370	228	61.9	38.1	1.099
7253 B	Greenwood	Sifted June	Small and slightly broken	Somewhat turbid	596	386	210	64.8	35.2	1.090
7254 B	Greenwood	Extra Sifted June	Nearly all slightly broken	Slightly turbid	598	379	219	63.3	36.7	1.063
7249 B	Polk's Best	Early June	Slightly sprouted and broken	Somewhat turbid	598	391	207	65.4	34.6	1.112
7250 B	Polk's Best	Sifted June	Slightly sprouted and broken	Somewhat turbid	586	370	216	63.0	37.0	1.072
7251 B	Polk's Best	Extra sifted June	Small—not much broken	Nearly clear	595	360	235	60.5	39.5	1.0218
7255 B	Polk's Best	Petit-Pois	Peas small—badly broken	Nearly clear	594	351	243	59.1	40.9	1.075
7256 B	Everybody's	Soaked Peas	Large and all broken	Liquor muddy	61	408	204	66.7	33.3	1.120

The appearance of the drained peas and liquor was quite variable. We would have expected the smaller and better grades of peas to have been less broken since they required less blanching. This, however, was not always the case. The liquor of the more mature peas showed a greater tendency to be turbid, due to the longer time required for blanching and the greater tendency of these peas to swell and burst.

TABLE II—PERCENTAGE COMPOSITION OF CANNED PEAS

Original basis										Water-free basis													
Protein N $\times 6.25$										Protein N $\times 6.25$													
Sample	Water	Crude starch	Sugar	NaCl	P <sub>2</sub> O <sub>5</sub>	Protein N $\times 6.25$	Crude starch	Sugar	NaCl	P <sub>2</sub> O <sub>5</sub>	Protein N $\times 6.25$	Crude starch	Sugar	NaCl	P <sub>2</sub> O <sub>5</sub>								
7246 B	78.52	4.56	11.94	1.15	0.40	0.167	21.23	55.8	5.35	1.86	0.777	7247 B	80.77	4.64	8.22	1.13	0.60	0.145	24.1	42.6	5.87	3.12	0.754
7248 B	84.55	3.31	8.11	0.71	0.40	0.106	21.4	52.5	4.59	2.59	0.686	7252 B	82.29	3.79	8.05	..	..	..	27.8	51.0	..	..	..
7253 B	82.90	..	6.50	..	..	..	..	38.0	..	..	..	7254 B	85.92	2.96	5.16	..	..	..	21.0	36.6	..	..	..
7249 B	81.65	4.55	9.18	1.97	0.53	0.131	24.8	50.0	10.68	2.34	0.713	7250 B	86.32	3.09	6.09	1.46	0.34	0.118	22.7	41.5	10.66	2.48	0.862
7251 B	88.06	2.85	3.30	..	..	..	23.9	27.6	..	..	..	7255 B	89.61	2.34	2.73	..	..	..	22.5	26.2	..	..	..
7256 B	78.96	3.95	9.87	1.32	0.73	0.165	18.7	47.0	6.27	3.47	0.784												

In a general way the gravity of the drained peas was practically the same as that of the fresh peas used in each brand. Samples 7254 B and 7246 B were exceptions to this rule. The gravity of the liquors was practically the same for all, the samples 7248 B and 7250 B having the minimum gravity. The salt and sugar content of these samples help explain this discrepancy.

## PERCENTAGE COMPOSITION

The chemical analyses were made on the liquor and drained peas independently. Considerable difficulty was encountered in working on the liquor. Owing to the fact that it would quickly ferment, it was necessary to evaporate it to dryness in order that

a number of samples might be run simultaneously. However, the samples assumed a dark color upon drying, especially those in which the starch content was low. The dried substance proved to be hygroscopic and caused trouble in weighing. All of this would indicate that when time permitted, it would be advisable to determine the liquors without drying which, of course, means that the sample must to a certain extent, be handled individually. In many cases on account of the small amount of liquor obtained, it was impossible to make all of the desired determina-

tions and to check some inconsistent results. In general, the methods of analysis used were those of *Bull. 107*, Bureau of Chemistry. In order to run a number of samples simultaneously, it was necessary to dry a large quantity of the drained peas and pulverize the dry sample until all would pass through a forty mesh sieve. From this dried material the samples for subsequent determinations were weighed out.

TABLE III—PERCENTAGE COMPOSITION OF PEA LIQUOR

Original basis										Water-free basis													
Protein N $\times 6.25$										Protein N $\times 6.25$													
Sample	Water	Crude starch				Salt				Sample	Water	Crude starch				Salt							
		Sugar										Sugar											
7246 B	92.9	2.11	1.68	1.95	0.55	0.086	29.78	23.7	27.5	7.8	1.22	7247 B	93.23	1.98	1.10	1.33	0.79	0.080	29.21	16.33	19.58	11	1.19
7248 B	96.54	1.06	0.77	0.76	0.54	0.048	30.65	22.27	21.89	15	1.39	7252 B	94.62	1.51	..	0.46	..	..	25.83	7.89	..	..	..
7253 B	93.87	..	0.56	..	..	..	..	..	..	..	..	7253 B	93.87	..	0.56	..	..	..	..	..	..	..	..
7254 B	94.66	1.37	..	0.16	..	..	25.59	3.00	..	..	..	7249 B	93.61	2.06	3.11	1.85	0.78	0.073	32.22	48.66	28.93	12	1.15
7250 B	95.42	1.38	1.52	0.58	0.54	0.071	30.37	33.15	12.72	11	1.55	7250 B	95.42	1.38	1.52	0.58	0.54	0.071	30.37	33.15	12.72	11	1.55
7251 B	95.22	1.53	..	0.04	..	..	32.38	0.93	..	..	..	7251 B	95.22	1.53	..	0.04	..	..	32.38	0.93	..	..	..
7255 B	95.02	1.41	..	0.11	..	..	28.27	2.35	..	..	..	7255 B	95.02	1.41	..	0.11	..	..	28.27	2.35	..	..	..
7256 B	91.80	1.70	1.7	1.85	0.93	0.123	20.71	20.7	22.6	11	1.51	7256 B	91.80	1.70	1.7	1.85	0.93	0.123	20.71	20.7	22.6	11	1.51

Tables III and IVA and B have been prepared showing the percentage composition of the drained peas and liquors on both the original and water-free basis. The composition on a water basis in a measure eliminates the abnormal figures that may result from varying amounts of liquor added. Table II has been calculated on the basis of the peas and liquor as they occur in the can. This table has also been reduced to a water-free basis.

The composition of the different samples varies quite as much as do the analyses made by Street and Dubois. However, all determinations come within the limits found by these authors.

According to the information given at the factory

the salt sugar solution used in all grades was 24 pounds sugar and 24 pounds salt to 500 gallons of water. This would mean that the liquor contained 0.57 per cent each of salt and sugar. This figure is hard to reconcile with the percentage of salt and sugar found in the pea liquor and canned peas. The maximum percentage of salt found in the liquor was 0.79 per cent in Sample 7247 B. The drained peas taken from the same can showed 0.52 per cent of salt, a figure by no means the highest in this table. The samples of liquor having the minimum salt content were 7248 B and 7250 B, each of which had 0.54 per cent. The drained peas from these cans had 0.32 per cent and 0.23 per cent, respectively, these figures being the smallest in the table. This would indicate a difference in the strength of the salt solutions used. This assists in explaining the low gravity of the liquor of these samples.

TABLE IVa—PERCENTAGE COMPOSITION OF DRAINED PEAS, ORIGINAL BASIS

Sample	Water	Ether extract	Crude fiber	Proteid N X 6.25	Sugar	Crude starch	Salt	Total ash	Salt-free	CaO	MgO	P <sub>2</sub> O <sub>5</sub>
7246 B.....	71.4	0.56	1.77	5.92	0.89	16.93	0.34	1.04	0.70	0.047	0.038	0.208
7247 B.....	75.81	0.38	1.74	5.74	1.14	11.04	0.52	1.10	0.58	0.053	0.033	0.172
7248 B.....	74.57	0.49	2.06	5.19	0.66	12.21	0.32	0.85	0.53	0.078	0.049	0.158
7252 B.....	74.69	0.49	1.98	5.21	1.22	14.74	0.64	1.27	0.63	0.053	0.038	0.179
7253 B.....	76.94	0.47	1.62	5.10	1.39	12.74	0.32	1.26	0.61	0.060	0.021	0.165
7254 B.....	80.85	0.53	1.74	3.89	1.31	9.72	0.65	1.33	0.41	0.061	0.040	0.128
7249 B.....	75.32	0.50	2.00	5.88	1.33	8.06	0.92	1.33	0.41	0.047	0.054	0.166
7250 B.....	80.96	0.50	1.99	4.10	1.44	8.86	0.23	0.67	0.44	0.047	0.035	0.147
7251 B.....	83.35	0.39	1.92	3.73	1.62	5.42	0.43	0.96	0.53	0.049	0.032	0.131
7255 B.....	85.85	0.42	1.54	3.16	1.85	4.56	0.58	0.95	0.47	0.031	0.036	0.142
7256 B.....	72.85	0.55	1.90	5.09	1.11	13.98	0.66	0.32	0.66	0.057	0.037	0.185

The highest sugar content of the liquor was in Sample 7249 B, being 3.11 per cent. The corresponding sample of drained peas had 1.33 per cent sugar, one of the highest of this table. The minimum sugar content was in liquor Sample 7248 B where it was 0.77 per cent. The corresponding drained peas sample had 0.66 per cent, the minimum of that table. Sample 7248 B especially seems to be deficient in these added constituents. We have no explanation of this save that the liquor is probably not made up according to formula. It has been suggested that selective absorption may play a part in determining the location of the salt and sugar added. This, however, is a field for further study.

TABLE IVb—WATER-FREE BASIS

Sample	Ether extract	Crude fiber	Proteid N X 6.25	Sugar	Crude starch	Salt	Total ash	Salt-free ash	CaO	MgO	P <sub>2</sub> O <sub>5</sub>
7246 B 1.96	6.18	20.7	3.1	59.2	1.16	3.65	2.49	0.17	0.134	0.730	
7247 B 1.59	7.18	23.71	4.7	45.65	2.19	4.55	2.36	0.22	0.142	0.714	
7248 B 1.94	8.09	20.41	2.61	55.87	1.29	3.34	2.05	0.35	0.198	0.639	
7252 B 1.93	7.84	20.58	4.81	48.16	2.55	5.02	2.47	0.21	0.157	0.716	
7253 B 2.03	8.03	22.11	6.01	42.14	2.82	5.48	2.66	0.26	0.093	0.675	
7254 B 2.77	9.08	20.33	6.83	42.07	4.86	6.85	2.09	0.32	0.203	0.640	
7249 B 2.07	8.09	23.83	5.35	52.91	1.66	3.94	2.28	0.19	0.223	0.667	
7250 B 2.64	10.43	21.54	7.54	46.52	1.20	3.34	2.34	0.25	0.178	0.738	
7251 B 2.32	11.55	22.41	9.68	32.53	2.22	5.75	2.53	0.29	0.188	0.784	
7255 B 2.94	10.91	22.36	13.10	32.24	1.13	6.69	2.56	0.21	0.223	0.854	
7256 B 2.03	6.92	18.51	4.02	50.85	2.40	4.79	2.39	0.21	0.157	0.756	

Liquors 7246, 47, 49 and 56 have very high starch content. These same liquors have the highest proteid content of the table. This is in a measure ex-

plained by Table I which shows all of these liquors to be "very turbid." The peas have been over-blanching or over-processed and have burst, allowing the solids including starch and insoluble proteid to become mixed with the liquor. It is also interesting to note that the gravities of these solutions have been increased to the highest of the table. The other factors of these tables vary so greatly that no fair conclusion can be drawn.

Table V shows the average composition according to the maturity of the pea. The Polk's Best Brand was made from the tender and more succulent peas—peas which have a gravity of less than 1.07, the Greenwood was made from the fresh pea harder than the Polk's Best Brand and having a gravity between 1.07 and 1.11, and the May Day from peas which sank in a 1.11 gravity brine. By means of this table (dried peas, original basis) we see the water decreases

from 81.37 per cent in the Polk's Best to 73.92 per cent in the May Day, the oldest peas. On account of the varying factor of water content no conclusion regarding other constituents from this table can be drawn.

According to the water-free basis calculations of the drained peas, the crude fiber decreased with the age of the pea, changing from 10.25 per cent in the youngest to 7.15 per cent in the mature peas. This fact is borne out by Street, who says: "The crude fiber of the immature pea, in which the meaty portion had just begun to develop, is usually higher than in the more mature."<sup>1</sup> Protein decreases slightly, 22.31 per cent to 21.74 per cent, as the pea becomes older. The crude starch increases from 41.05 per cent to 53.57 per cent.

The figures for the sugar content of these brands call for an explanation. Biting<sup>2</sup> gives the average sugar content of fresh peas as follows:

Grade	Original basis	Water-free basis
First, corresponds to Polk's Best....	0.88	4.51
Second, corresponds to Greenwood..	0.71	3.26
Third, corresponds to May Day....	0.55	2.16

These figures indicate that the sugar which forms in the pea during the early stage of growth does not keep pace with the other constituents as the pea matures. It has been suggested that the variation of sugar content of the drained peas was due to the sugar content of the liquor.

<sup>1</sup> Loc. cit.<sup>2</sup> U. S. Dept. of Agriculture, Bureau of Chemistry, Bull. 136



TABLE Vd—PERCENTAGE COMPOSITION OF DRAINED PEAS BASED ON BRAND  
ORIGINAL BASIS

Brand	Water	Ether extract	Crude fiber	Proteid N X 6.25	Sugar	Crude starch	Salt	Total ash	Salt-free ash	CaO	MgO	P <sub>2</sub> O <sub>5</sub>
May Day.....	73.92	0.47	1.85	5.61	0.89	14.06	0.39	0.99	0.60	0.059	0.040	0.179
Greenwood.....	77.49	0.49	1.78	4.73	1.31	10.17	0.74	1.28	0.55	0.058	0.033	0.157
Polk's Best.....	81.37	0.45	1.86	4.22	1.56	7.97	0.41	0.89	0.47	0.043	0.039	0.146

## WATER-FREE BASIS

May Day.....	1.83	7.15	21.74	3.14	53.57	1.55	3.85	2.30	0.25	0.158	0.694
Greenwood.....	2.34	8.31	21.01	5.55	44.12	3.54	5.78	2.41	0.27	0.151	0.677
Polk's Best.....	2.00	10.25	22.31	8.92	41.05	2.55	4.98	2.43	0.23	0.203	0.761

TABLE Vb—PERCENTAGE COMPOSITION OF CANNED PEAS BASED ON BRAND

Brand	Original basis					Water free basis					
	Water	Proteid N X 6.25	Crude starch	Sugar	Salt	P <sub>2</sub> O <sub>5</sub>	Proteid N X 6.25	Crude starch	Sugar	Salt	P <sub>2</sub> O <sub>5</sub>
May Day.....	81.28	4.17	9.42	1.00	0.47	0.139	22.2	50.3	5.27	2.52	0.739
Greenwood.....	83.70	3.37	6.60	..	..	..	24.4	41.87	..	..	..
Polk's Best.....	83.91	3.27	5.35	1.71	0.43	0.125	23.49	36.32	10.67	2.41	0.787

There are two points that lead us to believe this is not the case. *First*, the liquor of the sample 7249 B is abnormally high in sugar, but the drained peas of this can show only a normal amount of sugar. *Secondly* the Polk's Best Brand would before processing have the highest water content and would absorb a smaller amount of liquor upon processing. Therefore, unless selective absorption comes into play, the conditions cannot be laid to the composition of the liquor. The question is one open for study. The salt-free ash is slightly higher in the youngest pea.

Upon comparing the analysis of the sample of "Soaked Peas" with the above averages, it is found that it agrees quite closely with the May Day grade. The reason for this is quite apparent for as far as maturity is concerned these grades lie very close together.

Table VI shows the maximum salt-free ash content of 2.66 per cent and the minimum of 2.05 per cent with an average of 2.38 per cent. The alkalinity of the ash varies from 2.5 to 2.1 cc. N/10 HCl per gram

## SUMMARY

The investigation has shown that in a pack of peas put up by a single concern where the conditions are as nearly uniform as it is possible to make them in factory work, great variations of results in individual samples are found. A large number of samples are desirable for conclusive results.

There is considerable variation in the proportion of liquor and peas in the different grades of the product. The composition of the liquor of the canned pea is largely determined by the blanching and processing, and as the more mature peas require a longer period, we may expect to find this grade with turbid liquors of high starch and proteid content.

The young immature dried peas contain 18 per cent more water than the oldest grade.

The crude fiber decreases from 10.25 per cent to 7.15 per cent on the drained peas, water-free basis.

The per cent of sugar seems to decrease with maturity. The reason is not apparent and should be a field for further study.

The part played by selective absorption in determining the location of added constituents is one requiring further study. The change in ash is very slight. The composition of the ash seems to remain the same throughout the growth of the pea.

(Credit is due to C. F. Coffin, Jr., for much of the analytical work reported in this paper.)

LABORATORIES INDIANA STATE BOARD OF HEALTH  
INDIANAPOLIS

## ON THE VALUATION OF LIME-SULFUR AS AN INSECTICIDE

By HERMAN V. TARTAR  
Received January 10, 1914

At the present time, the object of the examinations made of samples of commercial lime-sulfur solution in different chemical laboratories throughout the country, is to ascertain data regarding composition. In many cases, simply the total lime content, total sulfur content and specific gravity are ascertained. Oftentimes, however, quantitative determinations are also made of the different forms of sulfur in combina-

TABLE VI—ASH OF THE DRAINED PEAS

Sample	Salt-free ash		Alk. of ash (°)	Percentage composition of ash		
	Water-free basis			P <sub>2</sub> O <sub>5</sub>	CaO	MgO
7246 B.....	2.49	2.1	29.3	5.7	5.4	
7247 B.....	2.36	2.4	30.1	9.4	5.9	
7248 B.....	2.05	2.3	31.1	17.1	9.6	
7252 B.....	2.47	2.2	29.0	8.5	6.3	
7253 B.....	2.66	2.2	25.3	9.9	4.0	
7254 B.....	2.09	2.2	30.5	15.4	8.7	
7249 B.....	2.28	2.3	29.2	8.5	9.8	
7250 B.....	2.34	2.5	31.5	10.7	7.5	
7251 B.....	2.53	2.5	31.0	11.6	7.3	
7255 B.....	2.56	..	33.4	8.1	8.6	
7256 B.....	2.39	2.4	31.6	8.8	6	
Maximum.....	2.66	2.5	33.4	17.1	9.8	
Minimum.....	2.05	2.1	25.3	5.7	4.0	
Average.....	2.38	2.3	30.2	10.0	7.2	

(°)Cc. N/10 HCl per gram water-free sample.

dry sample. The phosphoric acid remains fairly constant averaging 25.3 per cent of the total ash. The CaO varies from 5.7 per cent to three times that amount. The MgO ranges from 4.0 per cent to 9.8 per cent of the total ash. There seems to be no relation between the ash or any of its constituents and the maturity of the pea.

tion. Entomologists and horticulturists, making field experiments, generally use a gravity test only.

A large proportion of the lime-sulfur used is for insecticidal purposes. Consequently, examinations made in the valuation of the same should be quantitative determinations of those properties from which the spray derives its insecticidal value. Actual chemical composition is a secondary matter except in so far as it may be an indication or measurement of these properties. For this reason, the determination of specific gravity is perhaps of little value except in a very general way. Samples of lime-sulfur having the same specific gravity may not be alike in chemical composition nor in many other properties. For example, a sample having a low specific gravity may have a greater per cent of polysulfides than a sample having a somewhat higher specific gravity.

In this discussion of valuation, it is well first to consider the properties which give to lime-sulfur its insecticidal value. The most exhaustive investigation available is, perhaps, that of Shafer.<sup>1</sup> He showed that with scale insects, like San José scale, the calcium polysulfides present in the solution soften the so-called wax about the margin of the insect and, on drying, cause it to stick to the plant. In the cases tried, the insects stuck tightly enough to cause also the death of the young by sealing them under the scale covering of the mother. Shafer's work also strongly indicated that one of the principal, if not the principal, insecticidal effect of lime-sulfur solution, upon insects of the type mentioned, is its great power of absorbing oxygen, thus causing the treated insects to suffer because of an insufficient supply of this element. Other experiments made by Shafer showed that sulfur dioxide is not "formed in appreciable amounts from sulfur deposited by lime-sulfur except at temperatures much above those found under spraying conditions in the orchard." The liberation of this gas is, evidently, not in amounts large enough to make it of importance in any consideration of the insecticidal properties of the spray.

The work done by the Department of Entomology of this station<sup>2</sup> indicates clearly that the principal insecticidal constituents are the calcium polysulfides. Experiments tried with calcium thiosulfate on San José scale<sup>3</sup> showed this material to have but little, if any insecticidal value. Wellington<sup>4</sup> arrived at similar conclusions. Shafer's<sup>5</sup> results also indicated that the thiosulfate has a limited insecticidal efficiency.

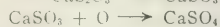
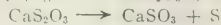
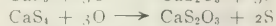
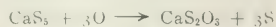
It has been known for long, too, that with certain insects, free sulfur has some killing power. It is stated that dry sulfur has been used in California perhaps a quarter of a century against almond-red spider. The experimental work carried on by the experts of the California Agricultural Experiment Station<sup>6</sup> and the Bureau of Entomology, U. S. Department of Agriculture<sup>7</sup> shows that towards certain

insects free sulfur has marked insecticidal properties.

There is also the possibility that hydrogen sulfide, a gas poisonous to insects, may be liberated from lime-sulfur when it combines with the carbon dioxide of the atmosphere or that given off in the breath of insects. So far as the writer knows, no means has been found to ascertain the extent to which this occurs. Experimental work carried out at this laboratory, however, indicates that if hydrogen sulfide is liberated under normal conditions it is in very small quantity, and, evidently, is not an important matter to consider here.

From the discussion preceding, it appears that, in general, the insecticidal properties of lime-sulfur are due principally to the following-named properties: (1) Its power to take up large amounts of oxygen, (2) its ability to soften the newly secreted wax at the margin of scale insects, and (3) the amount of free sulfur formed in its decomposition. If this be true, then the question of the correct valuation resolves itself into the quantitative measurement of these factors.

The amount of oxygen consumed depends upon reactions as represented in the following equations:



The combination of oxygen with the moist polysulfides is very rapid and quantities of the tetrasulfide or pentasulfide containing the same amount of calcium would absorb the same amount of oxygen and consequently produce the same amount of thiosulfate. This last named substance decomposes very slowly under ordinary conditions. For this reason, calcium sulfite is formed very gradually and the oxygen required to form the sulfate is absorbed slowly; too slowly, in the writer's opinion, to make it of insecticidal importance. Investigations made by the entomologist of this station indicate that calcium sulfite has practically no insecticidal effect upon San José scale.

The oxygen required to convert the polysulfides present in a given solution into thiosulfate can be estimated easily by use of the methods of Harris.<sup>1</sup> The titration used in the determination of "monosulfide" (for explanation of this term see bulletin referred to) sulfur may be used in estimating the amount of oxygen which will combine with the polysulfide present to form thiosulfate. In this case, 1 cc. of tenth-normal iodine is equal to 0.0024 gram of oxygen. The writer suggests that this oxygen-consuming capacity might be expressed as the "oxygen number" (analogous to the iodine number of fats), this term meaning the amount of oxygen consumed expressed as per cent of the lime-sulfur solution, or, in other words, the number grams of oxygen absorbed by 100 grams of lime-sulfur.

Free sulfur is liberated from lime-sulfur by reactions represented by the following equations:

<sup>1</sup> Mich. Agr. Exp. Sta. Tech. Bull. 6.

<sup>2</sup> Mich. Agr. Exp. Sta. Tech. Bull. 11.

<sup>3</sup> Unpublished results.

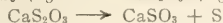
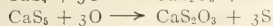
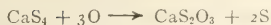
<sup>4</sup> "Biennial Crop Pest and Horticultural Report," p. 112 (1913).

<sup>5</sup> Mass. Agr. Exp. Sta. Bull. 116.

<sup>6</sup> L. ...

<sup>7</sup> Calif. Agr. Exp. Sta., Bulls. 164 and 234.

<sup>\*</sup> Private correspondence.



Since the oxidation of the polysulfide takes place rapidly there is a correspondingly rapid deposition of sulfur. The liberation of sulfur due to the decomposition of the thiosulfate is much less rapid. Considering everything, however, it appears that all of the sulfur liberated might be of equal insecticidal value; at least, there is no good evidence available to the contrary. The chemical estimation of the sulfur which will be deposited from a given amount of lime-sulfur solution can be made without difficulty. All of the sulfur present in the polysulfides in excess of that necessary to form the "monosulfide" of calcium combined in this form, would be deposited; also one-half of the sulfur present as thiosulfate in the original solution. The chemical methods for making these determinations have already been worked out in a thorough manner<sup>1</sup> and it is unnecessary to go into a detailed discussion of them here. The author suggests that the total free sulfur which would be deposited might be expressed as the "available sulfur number," this term meaning sulfur deposited expressed as per cent of the original lime-sulfur solution.

The third insecticidal property mentioned above is not so easily estimated. In fact, it is not definitely known why the spray solution softens the so-called wax on scale insects. It might be stated, however, that calcium thiosulfate is neutral in solution and gives no caustic effect on the hands, while solutions containing calcium polysulfide are very caustic. It is true that there is a small amount of calcium hydroxide in lime-sulfur solutions, due to hydrolysis of the polysulfide, but it is present in insufficient quantity to say that the caustic properties are due to the alkalinity of the solution. The writer's experience in handling the spray simply verifies the correctness of Shafer's statement that "the so-called caustic action of the wash on the hands seems rather due to its strong reducing power (power to absorb oxygen)<sup>2</sup> than to the alkalinity of the solution." It is very possible that this reducing power may also cause the softening of the so-called wax on the scale insects. If this be true, the "oxygen" number mentioned above would give its quantitative measurement. At any rate, the power of the spray to soften the so-called wax is evidently due to some property of the polysulfides and in the light of present knowledge no definite statement can be made regarding its exact nature nor its exact quantitative analytical measurement.

In conclusion, the writer wishes to state that the above discussion is merely a suggestion to chemists and entomologists. There may be other insecticidal properties of the spray than those mentioned and it is possible that the ordinary methods of valuation now in use are the best. If not, the discussion given here may prove to be of some value.

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<sup>1</sup> Jour Amer Chem Soc., 27 (1905), 244, THIS JOURNAL, 2 (1910).

271; Mich. Agr. Exp. Sta., Tech. Bull. 6.

<sup>2</sup> Words in parentheses inserted by the author

# A STUDY OF THE METHODS FOR EXTRACTIONS BY MEANS OF IMMISCIBLE SOLVENTS FROM THE POINT OF VIEW OF THE DISTRIBUTION COEFFICIENTS. I

By J. W. MARGEN

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It has been found by Berthelot and Jungfleisch<sup>1</sup> and later by Nernst<sup>2</sup> that when a substance is shaken with two immiscible solvents in which it is mutually soluble, that it always distributes itself between the two in a definite ratio.<sup>3</sup> They found, however, that this is true only when the molecular state of the solute is the same in both solvents, that is, when the substance does not polymerize in either solvent or polymerizes to the same extent in both, and that the ratio of the concentrations remains the same at a given temperature, irrespective of the amounts of solute present. It has furthermore been found that if there are two or more substances in solution, this ratio is the same as if each substance were present alone. This ratio is called the partition or distribution ratio for the particular solute and pair of solvents.

This ratio has been used in physical chemistry chiefly as a method for the determination of molecular weights and for the determination of chemical equilibrium. If, however, substances distribute themselves between two solvents always in the same ratio, it is easy to see that this ratio could be used to calculate the number of times that the one solvent must be shaken out with the other to extract all but 0.1 per cent of the material in question. If we let (*d*) = the distribution ratio, then in the case of ether and water, where the volumes are the same,

$$\frac{\text{concentration in water}}{\text{concentration in ether}} = \frac{C_1}{C_2} = \text{constant} = (d).$$

If we let (*a*) = the volume of aqueous solution,  
(*e*) = the volume of ether added,  
(*x*<sub>0</sub>) = the initial concentration in the aqueous solution and  
(*x*<sub>1</sub>), (*x*<sub>2</sub>), (*x*<sub>*n*</sub>) = the concentration after 1, 2, *n*, extractions,

then,

$$x_1 = d \left( \frac{x_0}{e} - \frac{x_1}{a} \right),$$

solving for *x*<sub>1</sub>, we get

$$x_1 = x_0 \left( \frac{da}{e + da} \right),$$

after a second extraction,

$$x_2 = d \left( \frac{x_1}{e} - \frac{x_2}{a} \right),$$

$$x_2 = x_0 \left( \frac{da}{e + da} \right)^2$$

after *n* extractions,

$$x_n = x_0 \left( \frac{da}{e + da} \right)^n.$$

From this it is to be seen, that although complete

<sup>1</sup> Ann. chim. phys., [4] 26 (1872), 396; Berthelot, *Ibid.*, p. 408.

<sup>2</sup> Z. physik. Chem., 8 (1891), 110.

<sup>3</sup> Nernst, "Theoretische Chemie" (1909), p. 494; Margen, "Physical Chemistry" (1908), p. 201.



separation is theoretically impossible, the number of shakings necessary to almost completely extract a substance depends upon the value of ( $d$ ).

The following example of the distribution ratio given by Partington<sup>1</sup> will serve to illustrate its use. For benzoic acid in ether and water, the value of ( $d$ ) = 0.0125 or  $1/80$ , that is, eighty times as much benzoic acid goes into the ether layer as goes into the water layer in one shaking, where equal volumes of each solvent are used. If we use 100 cc. of water ( $a$ ) and 20 cc. of ether ( $e$ ), then,

$$\frac{x_1}{x_0} = \frac{da}{e + da} = \frac{0.0125 \times 100}{20 + 0.0125 \times 100} = \frac{1.25}{21.25} = 0.0588 \text{ or } 1/17.$$

Only one-seventeenth, then, of the benzoic acid remains in the water layer after one extraction. After three extractions,  $(1/17)^3$ , or only  $1/4917$  remains. For succinic acid in ether and water, ( $d$ ) = 6, so that shaking but once,  $30/31$  of the acid is left in the water layer and, in order to wash out the succinic acid almost completely, it is necessary to shake out a great many times. This shows how different the distribution coefficient may be for different substances and that a detailed study from this point of view would throw much light upon the methods now in use for extraction by immiscible solvents.

In many of our quantitative "shaking-out" experiments there is a lack of definite directions as to the amount of ether or chloroform to use for each extraction, as to just how many times various solutions should be shaken out and a doubt as to the accuracy of the results. An example of this kind is cited in the very excellent paper on the examination of hydrogen dioxide solutions, *Bull.* 150, U. S. Bureau of Chemistry, in describing the method for the determination of acetanilid. "The acetanilid was determined by shaking a 50 cc. sample of hydrogen peroxide twice with ether and once with chloroform, combining the several extracts in a tared beaker and drying at 70° C." The authors state that this method yields about 95 per cent of the total amount of acetanilid present. There are no definite statements as to the volumes of ether or chloroform used in these experiments or as to the amount of shaking necessary for each extraction. The method of analysis for acetanilid will be discussed later in this paper.

Another example of the vagueness of this kind of estimation may be cited in *Bull.* 107 in the method for the "Approximate Quantitative Estimation of Saccharin." Here the analyst is referred back to the method for salicylic acid, where directions are given to extract with a "sufficient" amount of sulfuric ether. It is rather difficult for the analyst to know how much is a sufficient amount and furthermore, as will be shown later, what may be a sufficient amount for salicylic acid is not at all a proper amount for saccharin.

In this study, therefore, a few of the "shaking out" problems given in the bulletins of the U. S. Bureau of Chemistry have been attacked from the point of

view of the distribution ratio and, if better conditions were indicated by the experiments made, they were checked by analysis and modifications are herein suggested which have been found to give greater accuracy in these determinations.

The method for the determination of the distribution coefficient was similar to that given in laboratory exercises in physical chemistry.<sup>1</sup> Bottles, containing the solute and pair of solvents, were placed in a rack in a thermostat in such a way that the bottles were turned end over end at a rate of about thirty revolutions per minute for from thirty to forty minutes. The thermostat regulated at 25° C. (to less than 0.1° C. total variation, unless otherwise stated). The ether, chloroform or other solvent used was pipetted off after a run, allowed to evaporate over night, dried in a desiccator and weighed. After the volume of ether, chloroform or other solvent and the volume of the aqueous solution had been corrected for their solubility, the difference in weight between the weight found in the non-aqueous layer and the total weight was taken as the weight in the water layer. The solubility of ether in 100 cc. of water was taken as 7.8 cc. and that of water in ether as 1.2 cc. in 100 cc. of ether. The solubility of chloroform and of amyl acetate in water and *vice versa* was assumed to be negligible for our purposes. The method of calculation was the same as is shown above. The non-aqueous solvents were of U. S. P. strength. The acetanilid, saccharin, coumarin and other solutes were of Merck's best and had been carefully dried in desiccators. The results in this paper are stated in terms of volume rather than weight because volume methods of measurement are ordinarily used in analyses where this kind of extraction is necessary. A slide rule was thought sufficiently accurate in making these calculations, since there are many sources of error in this kind of determination and an indication of better conditions was sought by this method rather than absolute accuracy. In most of the determinations given below, when the concentration was widely varied, the distribution ratio could scarcely be called constant but within the limits found by actual analysis the results are very nearly so and certainly can be used to good advantage in this work.

#### ACETANILID IN HYDROGEN PEROXIDE

Shaking-out experiments were first tried with acetanilid in water and ether to find, if possible, the proper conditions under which we could get, by shaking out hydrogen peroxide solutions, not 95 per cent of the acetanilid, but 99.9 per cent. Hydrogen peroxide usually contains  $3/16$  grains of acetanilid per fluid ounce or about 0.04 gram per 100 cc. This amount was found to be very small to handle in the laboratory, so weights of acetanilid varying from 0.05 to 0.25 gram were used with 100 cc. of water and 50 cc. of ether. It was correctly assumed, as is shown later, that the extraction of acetanilid is practically the same from water as from 3 per cent hydrogen peroxide. These mixtures were shaken in 200 cc. bottles. Twenty-

<sup>1</sup> Getman, "Laboratory Exercises in Physical Chemistry;" Ostwald Luther, "Physico Chemische Messungen."

<sup>1</sup> "Higher Mathematics for Chemical Students," Van Nostrand & Co.

five cc. of the ether layer were pipetted off into small evaporating dishes, dried and weighed as described above. The following table shows the results obtained:

$$\left( \frac{C_1}{C_2} = d \right)$$

(1) Wt. acet used	(2) Wt. found in 25 cc. ether	(3) Wt. acet. in ether layer	(4) Wt. acet. in water layer	Wt. in 10 cc. water layer	Wt. in 10 cc. ether layer
Using 100 cc. of water, 50 cc. of ether and drawing off 25 cc. for (2)					
0.0863	0.0282	0.0475	0.0388	0.347	
0.1484	0.0482	0.0813	0.0671	0.350	
0.1492	0.0485	0.0818	0.0674	0.349	
0.2243	0.0770	0.1298	0.0945	0.310	
Using 100 cc. of water, 40 cc. of ether and drawing off 20 cc. for (2)					
0.1006	0.0302	0.0485	0.0521	0.346	
0.2001	0.0790	0.1020	0.0981	0.315	
Average, 0.336 = 1					

This means that if acetanilid is shaken up between equal volumes of ether and water, one-third of the acetanilid remains in the water layer. If 50 cc. of water, containing acetanilid, are shaken with 20 cc. of ether (assuming that the ether does not dissolve in the water) we find that on washing once,

$$\frac{1}{3} \times 50 = \frac{16.6}{36.6} = \frac{1}{2.2} = 0.454$$

of the original amount is left in the water layer, and after three such washings,

$$\left( \frac{1}{2.2} \right)^3 = \frac{1}{10.6} \text{ or } 0.0935$$

of the total amount remains in the water layer. Only 90.7 per cent of the acetanilid is extracted by the ether with this number of washings.

This calculation, like the latter calculations with water and ether, was made upon the assumption that the volume of water at equilibrium was 100 cc. and the volume of ether 42.2 or 32.2 cc. as the case might be, the data being given so that it can readily be recalculated. If the values given by Herz<sup>1</sup> are used for the solubilities and volumes of water and ether when saturated with each other, (d), in this case, is lowered to 0.313. In the later calculations with water, chloroform and amyl acetate, the volumes were assumed to be those originally taken.

Wt. acet. used	Wt. acet. found in 25 cc. chlor.	Wt. in chlor. layer	Wt. in water layer	$\frac{C_1}{C_2}$
0.0698	0.0328	0.0525	0.0173	0.132
0.0983	0.0460	0.0737	0.0246	0.134
0.1050	0.0498	0.0798	0.0252	0.126
0.1940	0.0924	0.1478	0.1462	0.125
Average, 0.129				

The shaking out of acetanilid from aqueous solutions with chloroform was next tried and the results are tabulated below. One hundred cc. of water and forty cc. of chloroform were used for a shaking. Twenty-five cc. of the chloroform layer were pipetted off, evaporated, dried and the residue weighed.

<sup>1</sup> Ber., 18 (1898), 2671.

If, therefore, 50 cc. of the aqueous solution of acetanilid and 20 cc. of chloroform are used for an extraction, then,

$$\frac{0.129 \times 50}{20 + 0.129 \times 50} = \frac{6.45}{26.45} = \frac{1}{4.1} \text{ or } 0.244$$

remains in the water layer after one washing.

If, in the determination of acetanilid in hydrogen peroxide solutions, the hydrogen peroxide is washed twice with ether and once with chloroform, as is suggested in *Bull. 150*, using 20 cc. at each washing, then

$$\left( \frac{1}{2.2} \right)^2 \times \frac{1}{4.1} = \frac{1}{20} = 0.05,$$

or 5 per cent of the acetanilid remains in the aqueous layer. The authors of *Bull. 150* state that they obtain about 95 per cent of the acetanilid present by this method. The calculation here checks well with their results.

It is to be seen that each washing with chloroform extracts the acetanilid much more completely than a similar washing with ether. Apparently, then, it is better to wash with chloroform than with ether throughout the entire experiment. If aqueous solutions of acetanilid are shaken out three times with 20 cc. of chloroform at each extraction, only  $\frac{1}{69}$ , or 1.5 per cent remains in the aqueous layer, and after five such extractions,  $\frac{1}{1160}$ , or less than 0.1 per cent remains.

Of course the same laws that govern the number of washings of precipitates govern the amount used at each washing, so that, if 10 cc. of chloroform are used at each washing instead of 20 cc., only 80 cc. of chloroform are necessary to remove more than 99.9 per cent from the aqueous layer, instead of a larger amount, as is the case when using 20 cc. to a washing. The validity of this was tried by dissolving weighed amounts of acetanilid in distilled water and shaking out with chloroform, using separatory funnels in the ordinary way. With five shakings, using 10 cc. each time, correcting for the residue left by the chloroform, etc., an average of 99.1 per cent of the amount added was obtained. The calculated amount which we should obtain is 99.1 per cent. The agreement here is even better than could well be expected in determinations of this kind because there is usually a loss around the stoppers of separatory funnels. On three extractions from 50 cc. of water, using 10 cc. of chloroform for each extraction, an average of 93.0 per cent of the total amount of acetanilid used was obtained. The calculated amount is 93.5 per cent. This gives an idea of about how closely the calculated value may be checked by analysis.

Estimations were also tried to prove the correctness of this calculation for hydrogen peroxide as well as for water and to show that this method can be used in quantitative determinations for acetanilid. Known weights of acetanilid were dissolved in 50 cc. of a solution of perhydrol diluted to 3 per cent hydrogen peroxide, which was previously known to contain no acetanilid or other substance which would shake out with chloroform. The acetanilid was shaken out five times with 10 cc. portions of chloroform, using separatory

funnels. At each shaking the mixture was thoroughly agitated for two minutes and then the two liquids allowed to separate. The results are as follows:

Wt. acet. started with	Wt. total residue	Wt. residue from 50 cc. chloroform	Corrected wt. of acet.	Percentage acet. added
at 0.2560	0.2550	0.0015	0.2545	99.0
at 0.2149	0.2147	0.0002	0.2132	99.2

Average, 99.1

Another chemist, by shaking out acetanilid from 1.5 per cent hydrogen peroxide in separatory funnels with only the ordinary precautions, obtained an average of 98.8 per cent of the acetanilid, under these conditions.

The effect of temperature on the distribution coefficient of acetanilid in chloroform and water is not very marked. At 19.70° C., it was found to be so nearly the same value as at 25° C. that it is not worth while to take this into consideration. This value for the distribution coefficient as previously given should be very nearly correct for any ordinary laboratory temperature.

A modification for the method for acetanilid in *Bull.* 150 is suggested in the light of these facts. For quick work 50 cc. of the hydrogen peroxide should be shaken out (for two minutes at each extraction) five times with 10 cc. of chloroform at each washing. This gives 99 per cent of the acetanilid present. If the hydrogen peroxide be washed eight times, 99.9 per cent of the acetanilid is extracted. The chloroform liquid should be allowed to evaporate over night at ordinary temperatures and then dried in a desiccator. Better results were obtained in this way than when an effort was made to hasten the evaporation by blowing or heating to 70° C. Also, blanks must be run to correct for the residue left by the chloroform upon evaporation.

#### ACETANILID, VANILLIN AND COUMARIN IN VANILLA EXTRACTS

As would be anticipated, the determination of acetanilid, unless carefully guarded, would undoubtedly cause trouble in the excellent Hess and Prescott method for vanillin, coumarin and acetanilid in vanilla extracts.<sup>1</sup> This method, as modified by Winton and Bailey,<sup>2</sup> directs that 50 cc. of the dealcoholized extract be shaken out once with 20 cc. and three times with 15 cc. of ether. Taking the distribution coefficient of acetanilid between ether and water as  $\frac{1}{3}$  and disregarding the solubility of the ether in the water, not more than 93 per cent of the acetanilid can be extracted in the ether fractions. If this is true, then our acetanilid determinations are not worth much in this method.

Wt. of vanillin	Wt. found in 25 cc. ether layer	Wt. in ether layer	Wt. in water layer	$\frac{C_1}{C_2}$
0.0811	0.0384	0.0647	0.0164	0.108
0.1169	0.0550	0.0927	0.0242	0.110
0.2058	0.0980	0.1655	0.0403	0.104

Average, 0.107

The distribution ratio was run on vanillin between 50 cc. of ether and 100 cc. of water and the above results were obtained.

<sup>1</sup> *Bull.* 107, U. S. Bur. of Chem.

<sup>2</sup> *J. Am. Chem. Soc.* 21 (1899), 286; 24 (1902), 1148; 27 (1905), 719.

When an aqueous solution of vanillin, therefore, is extracted three times with 15 cc. and once with 20 cc. of ether, as suggested by Winton and Bailey, the ethereal solution extracts all but 0.4 per cent to 0.6 per cent of the vanillin. This shows that the present method for the extraction of vanillin with ether is quite sufficient for our needs. The distribution ratio for coumarin, although it was not found to be very constant, and for that reason is not given here, is still less, about 0.0374. When an aqueous solution of coumarin is shaken out with ether by the above mentioned method, only a few hundredths of a per cent are left in the aqueous layer.

When the ethereal solution of vanillin was shaken up with 2 per cent  $\text{NH}_4\text{OH}$ , hardly enough vanillin remained in the ether layer to be a weighable quantity and so, for even small quantities of 2 per cent  $\text{NH}_4\text{OH}$  the separation is nearly complete with only one shaking. This, however, is not the case with coumarin or acetanilid. The distribution ratios for these two substances were determined between ether and 2 per cent, 3.58 per cent and 5.11 per cent  $\text{NH}_4\text{OH}$ . Although the ratios in these cases were not very constant as was the case with coumarin, the variation undoubtedly being due to a partial polymerization in the ethereal layer, yet a very good idea can be obtained from them regarding the separation of vanillin from acetanilid and coumarin with  $\text{NH}_4\text{OH}$  from this point of view. It was found that the ratio did not vary greatly with this change in the concentration of the  $\text{NH}_4\text{OH}$  with either. From this it would seem evident that the method proposed by Hess and Prescott where the vanillin is shaken out just once with the stronger  $\text{NH}_4\text{OH}$  and all removed, is preferable to the later method of Winton and Bailey. To reduce the number of shakings with  $\text{NH}_4\text{OH}$  is to reduce the amount of acetanilid and coumarin that go through with the vanillin. At best, in 5 per cent  $\text{NH}_4\text{OH}$  and ether, the distribution ratio for acetanilid is about  $\frac{1}{4}$  and for coumarin about  $\frac{1}{6}$ , so that, with one shaking of 10 cc. of 5 per cent  $\text{NH}_4\text{OH}$  and 50 cc. of ether 5 per cent of the acetanilid and 3 per cent of the coumarin go into solution with the vanillin. Winton and Bailey may have some other reason, however, which may make their method the more preferable.

#### SALICYLIC ACID, BENZOIC ACID AND $\beta$ -NAPHTHOL

The distribution coefficients of both salicylic and benzoic acids were run and in each case, between ether and water, the results were of such magnitude that under ordinary conditions, a very few washings remove practically all of either.

Beta-naphthol was tried between chloroform and water that had been made slightly acid with  $\text{HCl}$ . The distribution coefficient was found to be 0.071 which showed that with only a moderate amount of shaking out with chloroform practically all was extracted.

#### SACCHARIN

As has been stated, the method for saccharin given in *Bull.* 107 is rather vague and directs that the chemist extract with a "sufficient" quantity of sulfuric ether from aqueous solution, previously slightly acidified.



with HCl. The results on the distribution ratio run under these conditions, using 100 cc. of water, made slightly acid with dilute HCl, and 50 cc. of ether, are as follows:

Wt. of saccharin	Wt. found in 25 cc. ether	Wt. in ether layer	Wt. in water layer	$\frac{C_1}{C_2}$
0.0728	0.0260	0.0438	0.0290	0.267
0.1287	0.0492	0.0829	0.0458	0.235
0.1964	0.0738	0.1245	0.0719	0.245
Average,				0.249

Under ordinary conditions of extraction, four shakings with ether may be considered sufficient in a good many cases and in that of salicylic acid more than enough, but with saccharin, if 100 cc. of an aqueous solution of saccharin be shaken out four times with 20 cc. portions of ether, only 90 per cent of the amount present is removed. If the analyst desires to remove 99 per cent of the total amount present, it is necessary to shake out eight times with 20 cc. portions of ether, making 160 cc. of ether in all. If he uses 10 cc. instead of 20 cc. portions, which is more economical with the ether, it is necessary to shake out seven times to get 90 per cent and thirteen times, making 130 cc. of ether, in order to get 99 per cent of the total amount.

Experiments were tried to determine the distribution ratio between the aqueous solution of saccharin, made acid with dilute HCl, and chloroform, to see if the chloroform did not extract the saccharin better than did the ether. The results showed that the chloroform did not extract the saccharin nearly so well as did the ether and that it could not be used for this purpose.

A search was made to find an immiscible solvent which could be used to make a better separation from aqueous solution than did the ether. It was found that amyl acetate was a good solvent for saccharin and that it might be used for this purpose. It was also found by careful trial that amyl acetate can be easily evaporated from solutions of saccharin on a water-bath without loss. When saccharin was shaken out with 100 cc. of water, 5 cc. of concentrated HCl and 50 cc. of amyl acetate, the following value was found for the distribution coefficient:

Wt. saccharin used	Wt. in 25 cc. amyl acetate	Wt. in amyl acetate layer	Wt. in water layer	$\frac{C_1}{C_2}$
0.0745	0.0350	0.0700	0.0045	0.0306
0.1022	0.0478	0.0957	0.0065	0.0322
0.1838	0.0862	0.1724	0.0114	0.0315
Average,				0.0314

This would indicate that with four extractions from 50 cc. of aqueous solution of this strength of acid with 10 cc. of amyl acetate for each shaking, 99.9 per cent of the saccharin could be washed out. On three such washings, 99.4 per cent is extracted. This conclusion was tested by dissolving known weights of saccharin in 50 cc. of water, adding 5 cc. of 1-1 HCl and extracting with three portions of amyl acetate, using separatory funnels in the ordinary way. The results are as follows:

Wt. saccharin used	Wt. total residue found	Wt. residue in amyl acetate	Corrected wt. of saccharin	Percentage found
0.1020	0.1018	0.0006	0.1012	99.3
0.2045	0.2035	0.0006	0.2029	99.2

Average, 99.25%

These results check well with the calculated value of 99.4 per cent.

It was found that the distribution coefficient of saccharin between ether and water was decreased very much with increased concentrations of HCl in the aqueous layer. The distribution coefficient of saccharin between ether, water and HCl, using the same concentration of HCl as was used in the amyl acetate extraction, is given below:

Wt. saccharin used	Wt. saccharin in 25 cc. ether	Wt. saccharin in ether layer	Wt. saccharin in water layer	$\frac{C_1}{C_2}$
0.0751	0.0386	0.0651	0.0100	0.0618
0.1175	0.0602	0.1013	0.0162	0.0647
0.1816	0.0933	0.1575	0.0241	0.0613

Average, 0.0624

This is somewhat higher than the value for amyl acetate. From this it is to be seen that it takes four extractions with 10 cc. portions to accomplish what three of amyl acetate do. The ether is, however, more pleasant to handle and, moreover, on five such extractions, removes 99.9 per cent of the saccharin present.

Analyses were made with separatory funnels to check these conclusions, using 50 cc. of water, 2½ cc. of concentrated HCl and four 10 cc. portions of ether.

Wt. saccharin used	Wt. total residue	Wt. residue in ether	Wt. saccharin obtained	Percentage of total
0.1982	0.1978	0.0005	0.1973	99.5
0.1809	0.1806	0.0005	0.1801	99.6

Another analyst found by following the above directions and heating to 100° C. to remove traces of moisture and drying in a desiccator:

Wt. saccharin used	Wt. total residue	Wt. residue in ether	Wt. saccharin obtained	Percentage of total
0.1500	0.1489	0.0005	0.1484	99.0
0.1500	0.1489	0.0005	0.1484	99.0
Calculated amount,				99.4

The agreement here is not so good but when the fact is considered that the distribution coefficient varies several times over with the addition of only a moderate amount of HCl, it is evident that it is a question of the strength of the HCl as to the amount of saccharin extracted.

From this a modification of the present method for saccharin might be suggested. Fifty cc. of the aqueous solution are made acid with 2½ cc. of concentrated (38 per cent) HCl and shaken out four times with 10 cc. portions of ether, shaking for two minutes at each extraction. This gives at least 99 per cent of the saccharin and six washings, 99.9 per cent. This is true only when the concentration of the HCl is very nearly that specified. In these determinations a very small amount of HCl always goes into the ether layer and, since saccharin is a stable substance, it is recommended that, after the ether is all evaporated and the residue apparently dry, it be heated for a

few minutes at 100° C. in a water oven, cooled in a desiccator and weighed.

#### CAFFEINE AND TANNIN

In the method proposed by H. L. Smith<sup>1</sup> for the determination of tannin in tea, directions are that the caffeine be separated from the tannin by extraction from the aqueous solution with chloroform. The method<sup>2</sup> directs that 50 cc. of the solution be shaken out with four 30 cc. portions of chloroform, making a total of 120 cc. This method was tested from the viewpoint of the distribution ratio, using 105 cc. of water and 30 cc. of chloroform. The results are given below:

Wt. caffeine used	Wt. found in 20 cc. of chlor. layer	Wt. in chlor. layer	Wt. in water layer	C <sub>1</sub> C <sub>2</sub>
0.0653	0.0375	0.0563	0.0090	0.0456
0.1228	0.0698	0.1048	0.0180	0.0492
0.2061	0.1180	0.1770	0.0291	0.0470

Average, 0.0473

Hence, on one shaking with 30 cc. of chloroform, but  $\frac{1}{14}$  of the caffeine remains in the water layer. On four washings with 30 cc. of chloroform for each extraction, there is only  $\frac{1}{35,800}$  of the original amount left. This is, of course, beyond our limits of accuracy and such washing is unnecessary. Four washings, using 10 cc. for each extraction, are far more satisfactory and economical. Under such conditions, 99.7 per cent of the caffeine is extracted, using a total of 40 cc. of chloroform. If the aqueous solution is shaken out five times with 10 cc. portions of chloroform, 99.95 per cent is extracted. It might be pointed out that the aqueous liquid does not need to be made either acid or alkaline to get a good separation with chloroform.

The validity of the above is shown by the following analysis. Known weights of caffeine were shaken out from distilled water solutions with four 10 cc. portions of chloroform, the chloroform evaporated over night, the residue dried in a desiccator and weighed.

Wt. caffeine started with	Wt. total residue	Residue in chloroform	Wt. caffeine obtained	Percentage of total
0.0809	0.0816	0.0012	0.0804	99.4
0.1545	0.1547	0.0012	0.1535	99.3

This was repeated by another analyst with another sample of chloroform with these results:

0.2000	0.2005	0.0012	0.1993	99.6
0.2000	0.2002	0.0012	0.1990	99.5
		Calculated amount,		99.7

The distribution ratio of tannin between water and chloroform was also run. The chloroform solution, however, did not leave a weighable residue. Hence, error from this source need not be feared in this determination.

#### SUMMARY

I—A practical application of the distribution ratio has been made in a study of a few of the extraction methods given in the bulletins of the United States

<sup>1</sup> H. L. Smith, *Analyst*, **38**, 312; Chapman, *Chem. Abs.*, **2**, 1477; **4**, 1081.

<sup>2</sup> This method is not given in the bulletins of the United States Bureau of Chemistry but it is included in this paper as an example of somewhat excessive washing for the extraction of caffeine.

Bureau of Chemistry with the view of pointing out the fact that definite directions are needed in or extraction methods which give a definite amount of the material in question.

II—A modification of the method of analysis for acetanilid in hydrogen peroxide has been suggested.

III—The method for acetanilid, vanillin and coumarin in vanilla extracts has been discussed from the point of view of the distribution ratio.

IV—The methods now in use for salicylic acid, benzoic acid and  $\beta$ -naphthol have been studied and found satisfactory from this point of view.

V—A method has been suggested for the analysis of saccharin by extracting with amyl acetate and modification of the present method with sulfuric ether proposed which gives definite results.

VI—It has been shown in the analysis of caffeine (in the particular case referred to) that the amount of chloroform used for the extraction was excessive.

VII—The fact has been emphasized that a large number of extractions, using a smaller volume of solvent for each washing, is better than a fewer number of extractions using a larger amount.

A much more extended study of the methods of extraction is being carried on in this laboratory at the present time.

SOUTH DAKOTA FOOD AND DRUG DEPARTMENT  
VERMILION

#### SOME REACTIONS OF CHRYSOPHANIC ACID WITH REFERENCE TO ITS DETECTION IN COMPLEX MEDICINAL PREPARATIONS

By E. MONROE BAILEY

Received December 1, 1913

Chrysophanic acid, dioxymethylanthraquinone,  $C_{14}H_8O_4$ , is a yellow color principle of weakly acid character occurring in a number of medicinal plants notably in senna and rhubarb, and may be obtained also from its anthranol<sup>1</sup> chrysarobin,  $C_{18}H_{12}O_3$ , which is present in Araroba or Goa powder.<sup>2</sup> The presence of the free acid in plants is presumably due to the enzymic hydrolysis of the glucoside, chrysophan. Chrysophanic acid is not the active principle of rhubarb nor does the cathartic action of senna appear to be due, primarily, to its presence. It is soluble in alkalies with the production of a deep cherry-red color. The alkaline solution is heated with a little zinc dust, reduction takes place and the red color changes to yellow, the anthranol being formed.<sup>3</sup> Reoxidation of the alkaline solution takes place very readily; exposure to the air or simple dilution with water affects it as a drop or two of hydrogen dioxide produces the change almost immediately. It behaves as an indicator, although its merits as such do not appear to have been investigated.

Toward reactions of oxidation chrysophanic acid appears to be quite stable. When taken into the body it may be, apparently, eliminated unchanged in the urine. It is said that after the ingestion of senna the urine becomes intensely yellow and if rendered

<sup>1</sup> Liebermann, *Ber. d. chem. Ges.*, **1888**.

<sup>2</sup> Oesterle, *Arch. Pharm.*, **243** (1905), 434.

<sup>3</sup> Allen's "Commer. Organ. Anal.," 4th ed., Vol. V, p. 208; cf. "Alizarin,"

alkaline by sodium hydroxide a deep red color is produced. Of nine men in this laboratory, however, who took prescribed doses of senna—in preparations compounded with syrup of figs—in only two cases were positive tests given on examination of the urine twelve hours later.<sup>1</sup>

The applicability of chrysophanic acid for purposes of artificial coloring are apparent, one instance having been cited recently by Thum.<sup>2</sup> The sophistication of powdered rhubarb with powdered turmeric has been practiced and Howie<sup>3</sup> and others have given some attention to the detection of curcumin in such cases. In the inspection of patented and other medicinal preparations, the detection of chrysophanic acid serves to indicate the presence of a restricted group of vegetable constituents. And, finally, the similarity of many of its reactions to those of phenolphthalein, a substance of not uncommon occurrence in medicines, makes its detection in presence of that substance desirable.

If an alcoholic extract containing chrysophanic acid is dealcoholized or sufficiently diluted with water, acidified with a few drops of concentrated hydrochloric acid and shaken out with ether,<sup>4</sup> the coloring matter is taken up by the solvent and the ethereal layer is colored yellow. On washing the solvent with dilute alkali ( $2\frac{1}{2}$  per cent ammonium hydroxide was used) the color is transferred to the aqueous solution which is colored red. Similarly treated, picric acid and the color principle of hydrastis yield no red color to dilute alkali nor does their presence interfere with subsequent tests; but curcumin, haematoxylin, and phenolphthalein yield colors not to be distinguished in certain concentrations from that produced by chrysophanic acid. In the cases of curcumin and haematoxylin, however, the color of their alkaline solutions is slowly fugitive. After standing over night at  $40^{\circ}$ – $50^{\circ}$  the red element is entirely lost, but the red color of chrysophanic acid and phenolphthalein is persistent.

If this solution is now acidified and shaken out with ether, the interfering color principles, curcumin and haematoxylin, are eliminated. Their absence can be demonstrated by concentrating a portion of the ether shake-out on filter strips and testing as follows:

(1) Moisten one of the strips with a drop of strong hydrochloric acid. No pink color will be obtained, showing the absence of haematoxylin.

(2) Moisten another strip with a mixture of hydrochloric—boric acids. No red color will be produced, showing the absence of curcumin.

(3) Moisten a third strip with dilute ammonium hydroxide. A pinkish red color will indicate the presence of chrysophanic acid or phenolphthalein or both.

To eliminate phenolphthalein transfer a portion of the ether shake-out obtained above to a test tube and drive off the ether. Add a little zinc dust and 4–5 cc. of 25 per cent sodium hydroxide, boil until the red color is discharged and cool the solution. By this treatment chrysophanic acid is reduced, as already described, the solution becoming yellowish, and phenolphthalein is reduced to phthalin which is colorless. Dilute the alkaline solution with water or treat it with a few drops of hydrogen dioxide and the characteristic cherry-red color of chrysophanic acid will be obtained. Phthalin remains unoxidized under these conditions.

Curcumin and haematoxylin both undergo reduction by means of zinc dust and sodium hydroxide and neither are subsequently oxidized by hydrogen dioxide, but their yellow or brown solutions mask the color of chrysophanic acid in certain proportions and thus make the test for the latter less distinct. It is therefore best to eliminate these substances by the method described.

ANALYTICAL LABORATORY  
CONNECTICUT AGRICULTURAL EXPERIMENT STATION  
NEW HAVEN

## LABORATORY AND PLANT

### IMPROVEMENTS IN THE IODINE PENTOXIDE METHOD FOR THE DETERMINATION OF CARBON MONOXIDE IN AIR

By ATHERTON SEIDELL

Received January 10, 1914

The iodine pentoxide method is based upon the reaction  $I_2O_5 + 5CO = 5CO_2 + I_2$  which has been found to be quantitative at approximately  $150^{\circ}$ . The sample of air is passed first through absorption tubes containing potassium hydroxide and concentrated sulfuric acid and then through a U-tube containing powdered iodine pentoxide, and immersed in an oil bath heated to  $150^{\circ}$ . It is obvious that either the resulting iodine or the carbon dioxide may be used as the measure of the carbon monoxide.

<sup>1</sup> These tests were made with commercial laxative preparations in which senna was declared to be an ingredient. The amounts of senna in many cases may have been too small to give the physiological test.

<sup>2</sup> *Am. J. Pharm.*, **85**, 1, 19.

<sup>3</sup> *Pharm. Jour.*, Nov., 1873; also *Am. J. Pharm.*, **4** (1874): 1, 16.

<sup>4</sup> The emulsion which forms is readily destroyed by adding acetone.

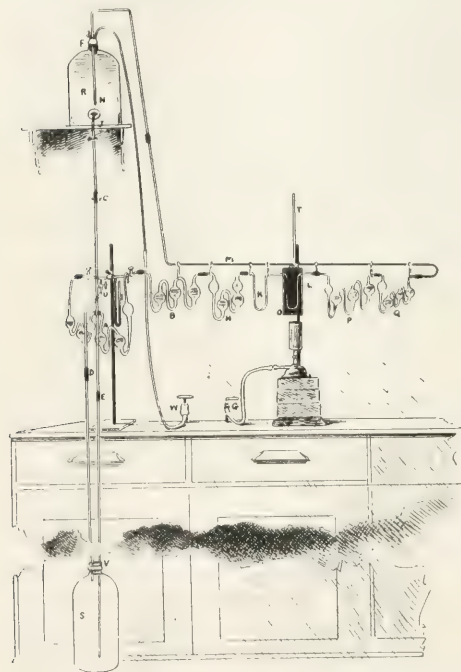
The apparatus as usually described<sup>1</sup> consists of a series of U tubes, spiral or other absorption tubes and potash bulbs connected with a suitable aspirator. On assembling an apparatus according to the usual descriptions, it became evident that a reduction of the dead air space would materially shorten the time required for a determination and reduce the correction factor resulting from the slight decomposition of the iodine pentoxide reagent by the air used to drive the sample through the apparatus. It was also hoped that the rate at which the sample is drawn through the apparatus could be increased.

The improved apparatus which has been developed is shown in the accompanying diagram. The essential feature of it is the special form of absorption

<sup>1</sup> Nicloux, *Compt. rend.*, **126** (1898), 746; Kincaid and Sanford, *J. Am. Chem. Soc.*, **22** (1900), 14; Levy and Pecoul, *Compt. rend.*, **140** (1905), 98; **142** (1906), 162; Morgan and McWhorter, *J. Am. Chem. Soc.*, **29** (1907), 1589; Weiskopf, *J. Chem. Met. Soc. S. Africa*, **9** (1909): 258, 306; and also *Chem. News*, **100** (1900), 191; Gautal, *Ann. chim. anal. appl.*, **15** (1910), 1–7; Levy, *J. Soc. Chem. Ind.*, **30** (1911), 1437.



bulb which has been adopted. A brief note on this bulb has been recently published.<sup>1</sup> As will be seen, the apparatus has been so arranged that the air sample is automatically transferred by water displacement from its container S to the reservoir R by way of the train of absorption bulbs and U tubes B, H, K, L, P and Q. The fixed level N of the end of the return tube M insures a constant hydrostatic pressure during the flow of the water from the upper to the lower bottle. The rate of flow is regulated by the screw pinch-cock C and the air pressure in the system, as indicated by the manometer I, is controlled by means of the cock U. The two sets of bulbs at A contain, respectively, concentrated sulfuric acid and aqueous KOH solution (1 : 1) for purifying the laboratory air used for washing the sample through the apparatus. Bulbs H con-



tain concentrated sulfuric acid. The upper of the double bulb at the right was filled with glass wool to prevent possible splashing of the acid into the U tube K which followed, and contained small lumps of potassium hydroxide. This U tube K and the following one L containing the iodine pentoxide were each made of a continuous glass tube and the two sealed together. The U tube L was immersed in the oil bath O. The iodine pentoxide was rather finely powdered and introduced in layers alternating with glass wool. Pure air was drawn through the tube heated to 150°–200° for several hours previous to beginning determinations upon air samples containing carbon monoxide.

The procedure for a determination is as follows: the reservoir R is filled by opening cock F, closing cock J and turning on the water at W. The stopper of the 2500 cc. sample bottle is replaced by the stopper V with its two glass tubes. These are then connected as shown at D and E. The carbon dioxide absorption bulbs B are then filled with 10 cc. of the stronger standard barium hydroxide solution (approximately 0.05 normal) and the bulbs Q with 10 cc. of the diluted standard barium hydroxide solution (approximately 0.005 normal). The bulbs P for retaining the iodine are filled with 5 cc. of 1 per cent aqueous potassium iodide solution plus 0.5 cc. of 0.5 per cent arrowroot starch solution. When all connections are made cock F is closed, the cocks J and U are opened and the screw pinch-cock C so adjusted that the water flows through at the rate of about two to three liters an hour. Although this is about six times as fast as Kinnicutt and Sanford specify, and three times as fast as Goutal prescribes for the apparatus described by him, there was no evidence of incomplete absorption of iodine at any time and only a slight loss of carbon dioxide in case of samples containing enough of this gas to nearly saturate the barium hydroxide solution.

The three volumetric solutions used for titrating the contents of the three absorption bulbs B, P and Q were, respectively, oxalic acid containing 5.6325 grams per liter (each cubic centimeter therefore corresponding to one cubic centimeter of CO<sub>2</sub> at 0° and 760 mm.), one-thousandth normal thiosulfate and oxalic acid solution of one-tenth the concentration of the stronger standard.

The standardization of the thiosulfate is made under conditions as nearly identical as possible with those under which the titration of the contents of bulbs P are made. Standard 0.001 normal iodine is prepared by dilution of a 0.1 normal solution and to quantities of this within the range of the amounts to be determined, is added enough potassium iodide to yield approximately 1 per cent of the latter and the titrations made to disappearance of the blue starch color with 0.001 normal thiosulfate. The choice of the 1 per cent concentration of potassium iodide was made on the basis of experiments with the absorption of iodine in bulbs P. Stronger solutions than 1 per cent caused the starch, which was added to assist in the retention of the iodine and as an indicator,<sup>1</sup> to flocculate in the form of blue granules. With larger quantities of iodine than encountered in the analysis of the samples of tunnel air it would probably be necessary to select other proportions of the several reagents than here specified for the particular conditions in hand.

In order to ascertain the degree of accuracy to be expected by the iodine pentoxide method a series of determinations was made with known amounts of carbon monoxide diluted with laboratory air. The carbon monoxide for this purpose was prepared by mixing concentrated sulfuric acid and sodium formate

<sup>1</sup> The absence of the blue color in the third of the series of three bulbs used for the potassium iodide starch paste reagent shows that the iodine has been completely retained in the first and second bulbs.

in a test tube and after displacement of the air in the tube, collecting the evolved gas over water. Successive dilutions of this were made and 10 to 100 cc. portions of the final mixture, corresponding to the volumes of carbon monoxide shown in Column 2 of the accompanying table, were introduced into partially evacuated 2500 cc. bottles and these samples, which contained from 36 to 360 parts of carbon monoxide per million, were drawn through the absorption apparatus as described above.

DETERMINATIONS UPON MIXTURES OF KNOWN AMOUNTS OF PURE CARBON MONOXIDE AND LABORATORY AIR

CO (at 0° and 760 mm.) per 2,500 cc. of air. Cc.	CO <sub>2</sub> BULBS B 10 cc. approx. 0.05 N Ba(OH) <sub>2</sub> used for each det.		IODINE BULBS P 5-10 cc. aq. 1% KI + 0.1% starch used for each det.		CO <sub>2</sub> BULBS Q 10 cc. approx. 0.005 N Ba(OH) <sub>2</sub> used for each det.	
	(COOH) <sub>2</sub> for excess of Ba(OH) <sub>2</sub> Cc.	Calc. CO <sub>2</sub> per 10,000 Cc.	thio for evolved I Cc.	Calc. CO (at 0° and 760 mm.) Cc.	excess Ba(OH) <sub>2</sub> Cc.	Calc. CO (at 0° and 760 mm.) Cc.
0.90			14.8	0.79		
0.456	2.6	13.0	7.65	0.405	2.15	0.345
0.456(a)	4.35	6.0	7.3	0.386	2.55	0.30
0.45			7.5	0.40		
0.229	3.3	10.2	4.0	0.207	2.8	0.28
0.229(a)	4.5	5.4	3.8	0.196	3.8	0.18
0.228	4.05	7.2	4.1	0.212	3.35	0.225
0.225			4.1	0.212		
0.225			3.95	0.20		
0.092	4.2	6.6	1.85	0.09	4.3	0.13
0.09			1.75	0.084		
0.09			1.75	0.084		
0.00	4.2	6.6	0.2		4.9	

(a) The mixture of CO + air stood over water two days before analysis. Factor for 0.001 N thiosulfate = readings  $\times 0.97 = 0.001 N$  exactly. 1 cc. 0.001 N thiosulfate = 0.056 cc. CO (at 0° and 760 mm.). 10 cc. approx. 0.05 N Ba(OH)<sub>2</sub> = 5.85 cc. (COOH)<sub>2</sub>; 1 cc. (COOH)<sub>2</sub> = 1 cc. CO<sub>2</sub> (at 0° and 760 mm.). 10 cc. approx. 0.005 N Ba(OH)<sub>2</sub> = 5.6 cc. (COOH)<sub>2</sub>; 1 cc. (COOH)<sub>2</sub> = 0.1 cc. CO<sub>2</sub> (at 0° and 760 mm.).

Blank determinations made by drawing 2500 cc. portions of laboratory air through the iodine pentoxide tube heated to 150°, gave blue colorations in bulbs P which required 0.2 cc. and sometimes as high as 0.4 cc. of 0.001 N thiosulfate for their discharge. These amounts, no doubt, correspond to the carbon monoxide normally present in the laboratory air and do not indicate a faint spontaneous decomposition of the iodine pentoxide. The correction of 0.2 cc. has therefore been applied to the thiosulfate titrations given in the table, since in these cases the estimation of the added carbon monoxide only was desired.

It will be observed that in the present experiments slightly low results for carbon monoxide were obtained in all cases. The amounts recovered varied from 88 to 98 per cent, the lower percentages being obtained with the higher amounts of carbon monoxide. Although on the percentage basis this appears to be a considerable loss, as a matter of fact when the very minute amounts of gas are taken into consideration the differences are quite small.

In regard to the carbon monoxide determinations based upon the titrations of the contents of bulbs Q it is seen that unaccountable irregularities are obtained. In most cases the amounts of carbon monoxide recovered were considerably lower than found by the iodine titration. It may, therefore, be concluded that

for the concentrations of carbon monoxide under consideration, no increased confidence in the results is to be obtained by using the carbon dioxide titration as a check upon the iodine titration.

HYGIENIC LABORATORY, WASHINGTON, D. C.

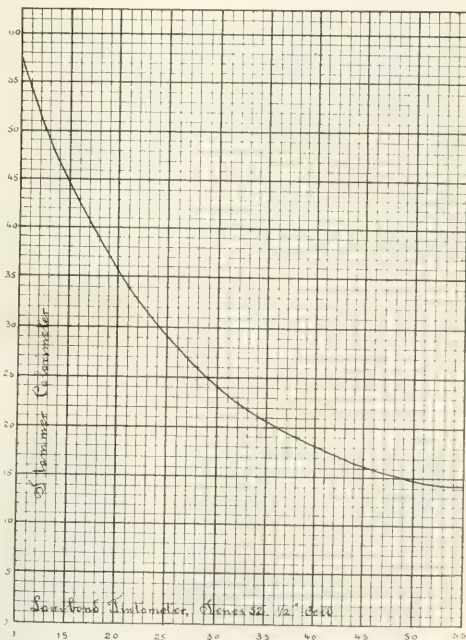
# CONVERSION CURVE FOR LOVIBOND'S TINTOMETER AND STAMMER'S COLORIMETER

By CARL A. NOWAK

Received January 20, 1914

In compliance with a request recently received asking me to construct a table correlating the readings taken on the Lovibond tintometer,  $\frac{1}{2}$  inch cell, series 52, and those obtainable with the Stammer colorimeter, I have carried out a number of comparative color determinations with these two instruments using an 8% malt wort, and plotted the results in a form of a conversion curve.

In order to verify the readings and to determine the extent of experimental error due to personal factors, such as variation in color vision, all readings



were taken by two persons, with the unexpected result, that in no case did the readings vary by more than 2 degrees Stammer or more than 0.2 to 0.3 degree Lovibond. All readings were taken at the same temperature, viz., 15 Centigrade. After plotting the tabulated results it was found that an almost ideal curve was obtained, showing that with a careful manipulation very slight differences in color can be detected with either of these instruments.

For the benefit of any who may not have access to both instruments and wish to convert the readings of

one into the other, the conversion curve, which is self-explanatory, is herewith given, inasmuch as, to the author's knowledge, a curve of this kind, or a table of conversions, is at present nowhere available.

CHEMICAL LABORATORY THE WM. RAHR SONS' CO  
MANITOWOC, WISCONSIN

#### APPARATUS FOR THE DETERMINATION OF FAT BY THE ROESE-GOTTLIEB METHOD<sup>1</sup>

By WILLIAM BRINSMAID

Wishing to use the Roese-Gottlieb method for the determination of fat in evaporated milk as published in Circular No. 66 of the Bureau of Chemistry, it was

found that the Röhrlig tubes for this purpose could not be purchased. None of the dealers in chemical glassware of whom inquiries were made, knew anything of them. The writer had seen the tubes designed by Mr. Patrick, but wished a tube differing from them in some respects.

As there is nothing complicated about these tubes, specifications were drawn up and the tubes ordered from the glass-blower. The specifications were determined by sealing the end of a glass tube of

five-eighths of an inch inside diameter and using the amounts of material required in exactly the same way as in an actual determination. After the mixture had settled for twenty minutes, marks were made on the tube in two places. The tube was first marked at the lowest point on the column of ether at which the ether could

and 85 cubic centimeters, respectively. The specifications were as follows:

1. Inside diameter of tubing to be five-eighths of an inch.
2. Drainage tube to be so placed that the bottom of the orifice is at the 19.5 cc. point.
3. Capacity of the tube to be 85 cc.
4. Mouth of tube to be constricted to fit the taper of a cork stopper.

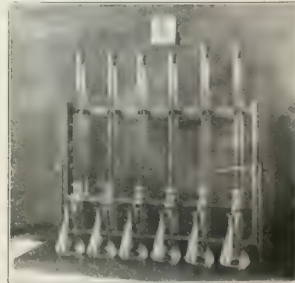
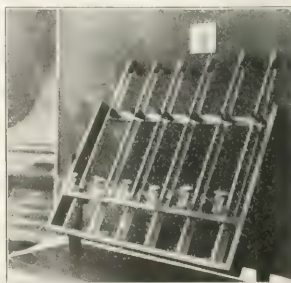
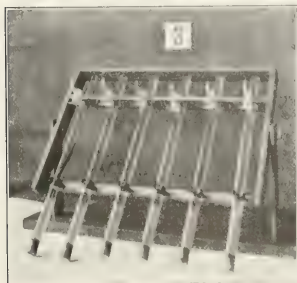
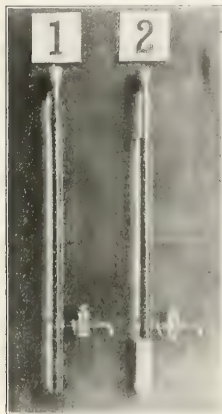
A rough drawing was sent with the specifications.

Fig. 1 shows an empty tube and Fig. 2 shows a tube with a fat determination in it. The height of the emulsion in the tube can easily be seen. With some milks the emulsion may stand a very little higher, but as yet there has been no difficulty with the tubes made as specified.

The tubes being awkward to handle and the drainage cock rather fragile, the problem of a safe and convenient mode of handling presented itself. At first the tubes were set in perforated blocks but when handled in this way the mixing has to be done singly and this is a rather slow method.

Finally a tilting rack was designed of the form shown in Figs 3, 4 and 5, and this has been found well adapted to the purpose.

Boiled cork stoppers are used in the tubes and if well fitted will hold the small pressure developed without trouble. The mixing of the milk with the ammonia and with the alcohol is done quickly while holding the tube in the hand and without using the stoppers. The tubes are then placed in the rack in an upright position and the ethyl ether added and the cork stoppers placed firmly in the tubes. The tilting frame with tubes is then turned back as shown in Fig. 3 and again turned to an upright position, and this continued as long as necessary. The petroleum ether is then added and the process repeated. The rack is then placed in the position shown in Fig. 4, the wing-nut tightened to keep it at this angle and the contents of the tubes allowed to settle. This position prevents



be safely drawn off. The second mark was made above the top of the ether column at a height that would allow space for proper mixing. The tube was then emptied and these two points were measured in cubic centimeters. They were found to be 19.5

the emulsion from running into the outlet tube, which is liable to do if the mixture is allowed to settle with the tube in an upright position.

In this way six determinations can be extracted in the time that would be required by one if held in the hand. Furthermore, as the tubes are not held in a warm hand, there is less pressure developed. After

<sup>1</sup> Presented at the 16th Annual Association of Food, Dairy and Drug Officials, Seattle, July 9-12, 1912.



settling for a proper time the rack is turned to an upright position, the flasks placed under the outlet cocks as in Fig. 5 and the mixed ethers and fat drained off. If closer drainage is desired the tubes may be held in the hand while the last portion is drained off. Funnels and filter papers may be placed in the flasks if desired.

STATE FOOD COMMISSION  
1623 MANHATTAN BUILDING, CHICAGO

### MODIFIED APPARATUS FOR THE PUTRESCIBILITY TEST

By A. M. BUSWELL<sup>1</sup>

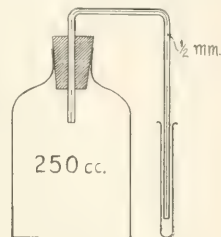
The putrescibility test as described by Jackson and Horton<sup>2</sup> is made in a 250 cc. bottle provided with a one-hole rubber stopper carrying a medicine dropper with a 5 cc. rubber bulb: 37-.5° C. is the temperature of incubation. The bulb is collapsed at the beginning of the test but soon becomes partially filled, due to the expansion of the liquid and the evolution of some of the gases originally in solution. Expansion is thus allowed for without permitting the absorption of air. It has been found, however, that the rubber bulbs deteriorate very rapidly. This not only makes the cost of up-keep of the apparatus high but

occasionally a test is lost, due to the failure of a bulb during incubation.

These facts led the writer to design for the putrescibility bottle the modified form of stopper shown in the figure. The modification consists in replacing the medicine dropper by a J shaped capillary tube of 0.5 mm. bore. The long end of the tube extends to the bottom of a small test tube which catches the overflow. The diffusion of gases through capillary tubing is so slight that the prevention of air absorption is effected. Aside from being more durable the modified stopper can be applied much more easily and rapidly than the old form and the convenience is quite an item when 50 to 100 bottles have to be made up at one time.

The modified stopper has been used in a series of comparative tests made by students in this laboratory and the results obtained so far are entirely satisfactory.

LABORATORY OF SANITARY CHEMISTRY  
COLUMBIA UNIVERSITY, NEW YORK



## ADDRESSES

### MODERN CHEMICAL INDUSTRY<sup>3</sup>

By FRITZ HABER

It is a special honor to me to speak here in appreciation of a man who recognized and represented the importance of physical thinking in applied chemistry at a time when almost without exception technical chemists declined to take this view.

Thirty years ago, when Hurter's activity was at its height, the center point of chemical industry was the Leblanc soda process. Here in England a number of technical methods for the manufacture of sulfuric acid and Glauber's salt, bleaching powder, soda, potash and the alkalis had been developed up to a remarkable standard. It is impossible to admire too much the richness of inventive genius and the clearness of judgment which the technical chemists of this period developed in your country. The world has learned of them how to convert chemical laboratory reactions into industrial technical processes and how to build up a system of analytical controls which enables the manager to follow the chemical change in a complicated system of reactions on a large scale.

The picture that technical chemistry exhibits to-day is quite different from that of thirty years ago. There is more brilliancy around the accomplishment of the organic than of the inorganic industries. The replacement of natural dyes by the products of coal tar, the extension of our medical resources by the manufacture of synthetic medicines, has gone far to extend the appreciation of chemical work and to produce the general conviction that chemistry is an inexhaustible field of economic possibilities. Indeed, one natural product after another falls into the domain of chemical synthesis, and chemistry is becoming the important factor in the economy of the tropical products which are used for industrial purposes. As soon as

the price of such a product exceeds a certain limit organic chemistry enters the field and synthesizes it in Western Europe. Thus indigo has succumbed to the onslaught of organic chemistry. Tanning materials at present are in a struggle with the condensation products of formaldehyde and phenolsulfonic acids. Camphor could maintain its position only by large price reduction, and the prospect of synthetic rubber holds down the would-be inflated prices of the natural product. The basis of this marked development in organic chemical industries is the combined working of science and technology. The fact and the success of this intermingling is so obvious that we need not dwell on the point.

In the territory of inorganic technical chemistry things are somewhat different. Here also a great change has taken place. The historical sulfuric acid and soda processes have lost much ground to the ammonia-soda and electrolytic processes, and to the contact process. New branches of industries have taken root and grown up. In this field, however, the connection between scientific and technical progress is neither so obvious nor so well recognized as in the realm of industrial organic chemistry. The reason is that the advance in inorganic science, during the last decade or two, has resulted less in the discovery of new facts which had direct technical applications, than in the unravelling and working out of new theoretical views. In fact, the introduction of physical laws and physical methods into the working sphere of inorganic chemistry has led to the greatest scientific progress. The invasion of physics into chemistry has produced the splendid development of physical chemistry, the basis of which is the second law of thermodynamics, the phase rule, and the theory of electrolytic dissociation. The introduction of the electroscope into chemical analysis has opened up the new chemical world of radioactivity. Now, in my opinion, inorganic chemical industries can gain almost as much by regarding their problems from a physical point of view as organic industries do by the application of structural considerations.

<sup>1</sup> Instructor in Sanitary Chemistry, Columbia University.

<sup>2</sup> THIS JOURNAL, 1 (1909), 328.

<sup>3</sup> The Hurter Memorial Lecture, delivered before the Liverpool Section of the Society of Chemical Industry, November 26, 1913 and printed in the *Jour. Soc. Chem. Ind.*, 33 (1914), 49.

I do not think it will be out of place in this lecture if I speak of one or two inorganic technical questions and lay stress on the physical considerations, which bear on them. I may be permitted to pass by many of the current examples of the part played by physical chemistry in technical chemistry, owing to their general recognition and go on to speak of a few industrial cases with which I have come in contact during the last year or two.

#### ZIRCONIUM OXIDE REPLACES STANNIC OXIDE IN THE ENAMEL INDUSTRY

During the last few years a not very obvious property of stannic acid has become the source of a new inorganic industry. Iron cooking utensils are coated on the inner side with a white enamel<sup>1</sup> which must contain no poisonous material; owing to its relative coefficient of expansion it must be very thin so as not to crack and chip away when the iron expands through rise of temperature. It must have a low melting point so that the iron does not lose its shape when it is coated with the melted enamel. A glass is therefore used which has nearly the following constitution: Borax, 26 per cent; quartz, 17 per cent; feldspar, 34 per cent; sodium silico-fluoride, 13 per cent; soda, 4 per cent; saltpetre, 3 per cent; kaolin, 3 per cent. The constituent parts are melted together; the fused mass is ground with water and some plastic clay to a thin paste of suitable thickness for even coating, then dried on the iron and heated to a temperature of 800° C. for about a minute, whereby fluxing of the enamel is attained. That is roughly the technology of enamelled iron. But such an enamel is too transparent, for the thin coating, which it is necessary to use on the iron, permits the dark color of the background to be seen. It is desirable to add something which, in small quantities, will render the enamel quite opaque, and which will, at the same time, give it a clear white color. The only satisfactory substance up to the present has been stannic acid. The requisite amount for a given surface is small, about one-half gram being required per square decimeter, but the employment of enamelled iron utensils is so great that 3300 metric tons of stannic acid are used yearly for this purpose. In earlier times about double the amount of stannic acid was used per unit area, as it was mixed and melted with the other constituents of the glass, and not, as at present, added to the enamel paste before the baking process.

The substitution of stannic acid by an equally efficient and non-poisonous, but cheaper clouding medium, has long been sought for by the enamel industry. Many and various substances have been tried and now it seems as if the problem has been solved.

The naturally occurring zirconium silicate is treated by alkali and a product of roughly the following composition is obtained:  $ZrO_2$ , 83 per cent;  $TiO_2$ , 4 per cent;  $SiO_2$ , 9 per cent;  $Na_2O$ , 2 per cent, the remainder being water. This impure zirconium oxide is replacing stannic acid. It is used in the same quantities and in the same way.

The development of this new industrial process has brought forward the question as to whether the specific property of the product is due to the oxide of zirconium or to some peculiar physical state that it possesses which could be imparted to other substances or perhaps to the impurities contained besides the oxide of zirconium. These questions are solved by some simple considerations.

Zirconium oxide is like tin oxide, namely, when in large crystals, a transparent colorless body. To render a glass opaque by the intermixture of particles of such a body the two substances must have different indices of refraction. The greater the difference, the greater will be the specific power of the particles to render the glass opaque. Now, the easily melted glasses

which are used for enamels have a coefficient of refraction in the neighborhood of 1.5. Natural tin oxide has the refractive index—for yellow light—of 1.9966 or 2.0799, according to the axis chosen. Its refractive power is therefore far greater than that of the glass. This property accounts for its utility in making enamels opaque.<sup>1</sup> Natural zirconium silicate has very similar refractive indices, being only about one unit smaller in the first place of decimals. Calculating from the well known additive properties of molecular refraction we find that the removal of the relatively feebly refracting silica from the zirconium silicate will increase its coefficient so that pure zirconium oxide will have a refractivity about 10 per cent greater than pure tin oxide. Thus we may expect that zirconium oxide with or without the above-mentioned impurities of the technical product acts like tin oxide if it is equally finely divided in the glass. Differences will, however, appear if one of the oxides dissolves in the enamel to a much greater extent than the other. The fact that only half the tin oxide is required when it is not melted with the enamel, but only mixed with it before roasting, shows that it is not so much a question of solubility, but of the rate at which it dissolves. Now the oxide dissolves only after the melting of the glass and the melting is stopped the moment the heat coming from above renders the surface mirror-smooth. Thus there is only time for a limited solvent action of the glass to take place. From this we gather that an equally small quantity of suitably calcined zirconium oxide or of tin oxide will probably render the enamel equally opaque. With voluminous zirconium oxide prepared by heating pure commercial zirconium nitrate to 800°, this conclusion was easily proved by a few experiments. Some minor points about the composition of the enamel would have to be considered if we would go into the subject more fully.<sup>2</sup> The former difficulty of finding empirically a substitute for tin oxide is now made plain by inspection of a table of refractive indices, because we find that the oxides of tin and zirconium have peculiarly large indices among the substances which are colorless, stable at high temperature and non-poisonous. The oxide of titanium which forms a small part of the technical product would be even better alone, because of its still larger refractive index, but the enamels made opaque by it show a yellowish color.

#### MESOTHORIUM FROM MONAZITE SAND

I will now pass from the zirconium oxide to its accompanying mineral monazite sand and speak for a moment of a new factor in its industrial treatment. Since the introduction of the Welsbach mantle for lighting purposes, monazite sand has been worked up in large quantities for the production of thorium nitrate. In the last two years a new and very peculiar question has arisen for this industry by the demand of the medical profession for radioactive substances which give penetrating  $\gamma$ -rays. There are in a thousand metric tons of the usual monazite sand containing 5 per cent of thorium oxide, according to the current radioactive figures, 18 milligrams of such a radioactive substance. The value of these few milligrams in a sufficiently concentrated form exceeds the value of any other substance known and covers the original cost of the 1000 tons of monazite sand. Now, the problem was to get these few milligrams out of the thousand tons in the normal thorium extraction process. This extremely valuable substance is the mesothorium I, of Dr. Hahn, which by changing into mesothorium II, becomes a much more powerful source of  $\gamma$ -rays than radium itself in equilibrium with its products.

<sup>1</sup> So far as I am informed, this view is not mentioned in the literature of enamel. But I have recently found that Wilhelm Ostwald, in his "Malerbriefe," Leipzig, 1904, explains the property of white lead of giving the greatest opacity for painting by help of the analogous consideration for oil and carbonate of lead.

<sup>2</sup> See Paul Randau, "Die Fabrikation des Enamels und des Emailierens," Wien und Leipzig, 1909; Julius Grauwald, "Theorie und Praxis der Bleich- und Gussemailindustrie," Leipzig, 1908, and "Chemische Technologie der Email-Rohmaterialien," Dresden, 1911; further "Ausgewählte Kapitel aus der Emailiertechnik," herausgegeben von der Redaktion des Sprechsaals, Coburg, 1912.

<sup>3</sup> See D. R. P. 189,364; Bela Havas "Ueber Eisenblechemaille," Karlsruhe, 1910 (Doctor-Dissertation); Hartmann, "Zirkonemail," München, 1910 (Doctor-Dissertation); Weiss, *Zeitschrift für anorganische Chemie*, 65 (1910), 218.

The problem is solved by the addition of 0.1 per cent, of barium to the sand before treating it with sulfuric acid in the usual way. In due course we get a radioactive deposit of barium sulfate rendered impure with  $\text{SiO}_2$ ,  $\text{TiO}_2$ , lead, and rare earths. These impurities must be separated by four distinct chemical processes, resulting finally in the regaining of barium sulfate with radioactive impurities only. This product is then concentrated by the ordinary methods using the chloride, carbonate, and bromide of barium, up to the  $\gamma$ -ray activity of pure radium bromide, or in excess thereof. One might certainly expect from such a complicated process that the largest part of the 18 milligrams would be lost. The real result, however, is found by comparing, using the  $\alpha$ -ray method, the amount of mesothorium in the final concentrate and in thorium in equilibrium with its transformation products. Dr. Keetman and Dr. Mayer have done so<sup>1</sup> and obtained the astounding result, that the figures are nearly the same. How is that to be explained? The sand always contains a small amount of uranium (say 0.1 per cent) and in consequence its equivalent of radium, which is saved together with the mesothorium. The amount of radium in the sand and in the final concentrate is determined by using the emanation method of estimation. Keetman and Mayer have also made this comparison and found an equally quantitative agreement. This yield also is almost theoretical. The quantity by weight of the radium is much greater than that of the mesothorium in the sand as well as in the final product. The final radioactive product of the 1000 tons shows a  $\gamma$ -radiation equivalent to 2200 milligrams of  $\text{RaBr}_2$ , three-tenths of which come from the bulk of real  $\text{RaBr}_2$ , while seven-tenths are due to the small admixture of the much more powerful mesothorium bromide. We have learned from Soddy and Fajans that radioactive elements occurring in the same place of the periodic system are inseparable by any chemical means. Therefore, according to this rule, the quantitative extraction of mesothorium follows from the quantitative extraction of the larger mass of radium. That the latter accompanies the barium fully is usually explained by the greater insolubility of the radium sulfate and their isomorphism.

I wonder whether this explanation will be final. Perhaps adsorption plays an important part, even in case the sulfates should be able to dissolve into each other in the solid state like alcohol and water in the liquid state. Diffusion is so extremely slow with solids that the surface phenomena become more prominent in all rapid changes. The work done by Ritzel<sup>2</sup> here at Liverpool, in this laboratory on the suggestion of Donnan induces us to regard adsorption as the primary step even in the case that a solid solution can be formed. Now there are certain facts stated quite recently by Fajans and Beer,<sup>3</sup> which suggest a near connection between adsorption and chemical affinity. On the other hand we have learned from Bragg's new brilliant investigations, that the ordinary solid crystalline salts are not systems in which one anion and one cation form a molecule which is separated from the next, but that one cation is probably bound to all the surrounding anions and one anion to all the surrounding cations. In consequence of that, we may feel inclined to consider the possibility of chemical forces acting between the atoms or ions in the surface of the solid precipitates and the molecules or ions in the final layer of the surrounding liquid, *i. e.*, in the adsorption layer. We may remember that there are good reasons for the belief that chemical forces are of electrical character and we know from electro-osmosis and similar phenomena that electrical forces are always acting between the surface of the solids and the adjacent layer of fluid. Adsorption phenomena, which are especially instructive with radioactive substances, owing to our being able to detect the presence of minute quantities, may thus perhaps be brought in close connection with chemical affinities.

## COMPARISON OF BLAST LAMP AND BUNSEN BURNER

The working up of the rare earths presents many physical-chemical points of interest. It is tempting to speak of the electrolytic preparation of the so-called "Mischmetall" containing 80-90 per cent cerium (the rest consisting of didymium and lanthanum) and its use for patent lighters, or about the manufacture of pure fluorides of the rare earths used for the salted arc to make the light white, or of the special properties which a thorium nitrate must show in order to give good Welsbach mantles. I will just consider one point more in detail because it is a good example of how the same simple consideration elucidates problems in very different branches of chemical working. The splendid reasoning of Le Chatelier explained the property of the Welsbach mantle in producing more light when heated by a Bunsen flame than any other radiator, as being due to the fact of the transparency of its substance in the infra-red region. In virtue of this transparency the mantle is unable to give off the heat imparted to it by the burning gas by the emission of heat wave energy. At the same temperature the Welsbach mantle radiates no more light than other substances, but in a given flame it gets hotter and more nearly approaches the temperature of the flame than does any other substance owing to this lack of heat radiation. From this state of things high light economy results, as we get with gas of a heating power of 5000 calories, one Hefner candle-power for an hour with the consumption of 0.8-0.9 l. of coal gas using the inverted type of burner which, as is known, affords a certain amount of previous heating. Now, by using a compressed air burner we can increase the economy to 0.6 liter of gas per Hefner candle-power with the same gas without more previous heating than in the former case. At first sight we may be led to think that the compressed air flame is hotter, but on closer consideration it will be evident that this is wrong. A Bunsen flame consists of two extremely thin reaction zones, the internal cone and the external one, the latter being used for heating the Welsbach mantle. In the internal cone the admixed air burns in an excess of gas, while in the outer cone the burning components undergo complete combustion with the air, forming  $\text{CO}_2$  and water. The position of the outer cone is fixed by the fact that in this zone the quantity of oxygen present must be exactly the theoretical amount required for complete combustion. Here, as there is no excess of air, the temperature depends only on the calorific value of the gas and the specific heat of the products of combustion, and is therefore at the maximum attainable with this gas and air. Thus the temperature of a blowpipe, using air, and gas of the same composition cannot exceed this maximum. Nevertheless, the mantle does get hotter in the blowpipe as is proved by the fact of increased economy. We do not even need this special observation of the mantle, as everyone knows from elementary experience that things can be heated to a much higher temperature in a blowpipe than they can in a Bunsen flame. Now, why is this the case? An explanation has been suggested in the fact that as the blowpipe has a smaller flame, the production of heat takes place in a more confined region. But this fact is really no explanation as we do not heat a geometrical space, but a quantity of gas, and we have just proved that it is impossible to get it hotter than it becomes in the outer cone of a Bunsen flame. To find the proper explanation we must consider a phenomenon that has no very obvious connection with this subject, namely, the dissolving of crystals in water. On this subject we have the theory inaugurated by Noyes and Whitney, and developed by Nernst, which states that the layer of liquid in contact with the crystal always consists of saturated solution. This saturated layer is continually losing its dissolved substances to the unsaturated further removed layers and at the same time being resaturated from the surface of the crystal. If the liquid is stirred this surface layer remains without motion, as the external friction is very much greater than the internal, while the neigh-

<sup>1</sup> Private communication.<sup>2</sup> *Zeitschrift für physikalische Chemie*, **67**, 724.<sup>3</sup> *Berichte der deutschen chemischen Gesellschaft*, **46**, 3408



boring layers have progressively increasing velocities. Now, for the sake of simplicity we may imagine this system of layers of increasing velocities replaced by a stationary layer in contact at one side with the crystal and on the other with the bulk of the solution uniformly moved by the stirrer. Thus, this stationary layer is a region through which diffusion of the dissolved substance takes place and the rate of solution is determined by the amount of substance which diffuses in unit time through this layer. The quicker the stirring is, the thinner is the stationary layer, the shorter is the distance for diffusion and the greater the rate of solution. Bearing in mind that diffusion and conduction of heat are entirely analogous processes, and that both phenomena follow the same differential equations, we at once arrive at the theory of the blowpipe, by introducing this simplifying conception of a stationary layer of gas on the surface of the heated body immersed in the rapidly moving gases of the flame. We see that the temperature of the solid body depends on the gain of heat by conduction through this stationary layer of gas and upon the equally large loss of heat due to radiation. The quicker the flow of the gas, the thinner will be the stationary layer; the thinner the layer, the greater will be the flow of heat and the higher the temperature of the body. Thus the difference in the velocities of the hot gases at equal temperature accounts for the higher efficiency of the blowpipe.<sup>1</sup>

The study of flames and the process of combustion and the possible uses of the products of combustion constitute a favorite field for a physical-chemical consideration.

#### MANUFACTURE OF FORMIC AND OXALIC ACIDS

Among the processes for utilizing the products of combustion in chemical industries, the action of generator gas on alkaline solutions stands out. The old method of making oxalic acid was by the action of fused alkalis on wood, and formic acid was got by splitting off of CO<sub>2</sub> from the oxalic acid. To-day these processes have disappeared. Formic acid is obtained by the action of carbon monoxide, in the form of generator gas, on alkali, and oxalic acid is made from formic acid by heating its salts and decomposing them into hydrogen and salts of oxalic acid. Berthelot discovered this action of CO on alkali as long as 50 years ago and has done much research on this subject. His view was that the caustic alkalis combine with CO best in presence of a little water but always at a very slow rate. In order to quicken up the reaction later on, CO at high pressure was used and Berthelot's concentrated solutions were replaced by solid alkali. This was developed into a technical process in which wet generator gas under pressure acted upon slowly shaken pieces of solid alkali; but finally it was found more expedient to replace the solid alkali by a dilute solution which has the surprising property at high temperature of acting much more quickly than concentrated solutions. This is the most modern form of the technical process.

This reaction has been studied in my laboratory.<sup>2</sup> The question was first whether the reaction goes on between water vapor and gaseous CO, or between dissolved CO and the constituents of the solution. Experiment proved the latter to be the case. Thus the speed depends upon the concentration of the dissolved CO which is used by the reaction and replaced from the atmosphere above. Under equal conditions of stirring and temperature the speed is strictly proportional to the partial pressure of CO in the gas room. At low temperatures the reaction is extremely slow, and moderate stirring of the gas and

solution is all that is required to keep the solution saturated with CO. Stronger stirring is without influence. Under these circumstances a high concentration of alkali helps to a comparatively rapid chemical change, but the reaction velocity is always far below that required for a technical process. Heating, as usual, increases the reaction velocity very much, and above 100° it becomes difficult to keep the solution saturated with CO by stirring. At 160° to 170° we cannot arrive at a point where stronger stirring would not materially increase the progress of the reaction. In this region of temperature the velocity of reaction meets the technical requirements, provided the absorbing liquid is brought into extremely close contact with the current of generator gas. Concerning the influence of the concentration of the alkali upon the speed of reaction, we find that from 100° upwards solutions containing about 10 per cent of alkali become more and more marked by a high rate compared with stronger as well as weaker solutions under the same conditions of temperature and stirring. At 160°, for instance, the 10 per cent solution works 15 times better than a 43 per cent one. The suggestion that the 10 per cent solution becomes best intermixed with the gas by the stirrer in virtue of an especially small surface tension is not supported by measurements of this constant at high temperature,<sup>1</sup> and this point remains unsettled for the present. The older form of the process which works with solid alkali and the newer using the solution are seen now in very close connection. In the older form the gas used in a wet state produces by virtue of its water vapor a thin coating of concentrated solution of caustic alkali on the surface in which the CO dissolves and reacts as it does in the new process. Perhaps this industrial application illustrates very effectively the influence of temperature and stirring upon reaction velocity. Is it not remarkable that the same alkali which helps us so often to separate CO<sub>2</sub> from CO by the formation of carbonate in gas analysis is able under other conditions to separate perfectly the CO from the nitrogen of the generator gas?

#### FIXATION OF NITROGEN

Returning to the subject of flames we find that there is to-day much interest connected with the question of the possibilities of developing their power of fixation of nitrogen. Our usual flames give only very small traces of nitrous products by burning in air at ordinary pressure. In the case of the acetylene flame, which is very hot, a distinct yield can be obtained under ordinary pressure by the combustion with an air enriched with oxygen.<sup>2</sup> With other gas flames the combined application of air enriched with oxygen and of high pressure in the combustion chamber produces the same effect.<sup>3</sup> The interest in the utilization of this behavior for the production of nitric acid results from the fact that the question of fixation of nitrogen is a very burning one. It may be interesting to look more closely into this problem. The more the agricultural conditions in the world develop in such a way that the agricultural products are not used in the place of their growth, the greater becomes the necessity for the addition of fixed nitrogen to the soil. Plants take up fixed nitrogen from the soil and animals get it from the plants, both without increasing or decreasing its quantity; but if corn and meat are exported from the place of production, the ground does not regain the nitrogen which it has given up.

It is true that there is a certain natural replacement of nitrogen. In the track of lightning, free nitrogen is fixed to a certain extent and the rain carries it down from the atmosphere into the soil. Besides this there are, in the soil, nitrifying bacteria which transform free nitrogen into the fixed state. But they are very sparsely distributed, and there seems no way of increasing their number. The earlier rational agriculturist made use of the special

<sup>1</sup> See Haber and Le Rossignol, *Zeitschrift für physikalische Chemie*, **66**, 195. The influence of the rate of flow of the flame gases upon the temperature of an immersed body has first been mentioned by Perv. *Compt. rend.*, **137**, 909; see Haber, *Zeitschrift für physikalische Chemie*, **68**, 752.

<sup>2</sup> Friedrich A. Weber, "Ueber die Einwirkung von Kohlenoxyd auf Natronlauge" (Doctor-Dissertation), Karlsruhe, 1908. Gorton R. Fonda, "Ueber die Einwirkung von Kohlenoxyd auf Laugen" (Doctor-Dissertation), Karlsruhe, 1910.

<sup>1</sup> Unpublished results.

<sup>2</sup> See Haber and Hodsman, *Zeitschrift für physikalische Chemie*, **67** (1909), 383.

<sup>3</sup> See Haber and Coates, *Zeitschrift für physikalische Chemie*, **69** (1909), 337; Wolokitin, *Zeitschrift für Elektrochemie*, **16**, 814.

property of leguminosae which grow nitrifying bacteria on its root nodules. These natural aids are now insufficient. The yearly deficit in fixed nitrogen is characterized by the fact that the world's demand for fixed nitrogen amounts to three-quarters of a million tons, by far the largest consumer being agriculture. Nowadays, this requirement is supplied mostly from two sources: the main bulk from the Chilean fields in the form of saltpetre and a smaller part from coal in the form of ammonium sulfate. A few years ago anxiety arose whether the Chilean fields would be sufficient to meet the ever-increasing demands for more than a few years to come. To-day we are confident that they will last at least till to the middle of our century, even at the present rate of increase of demand. But when we are told that the Chilean factories have replaced their old and primitive methods by new and very efficient ones and at the same time see that the price continues on its upward course, we realize that the richest and most accessible seams have been exhausted. Therefore, the economic future does not look very cheerful, unless a powerful rival step in.

In regard to the natural store of nitrogen in coal which averages a little over 1 per cent, it is obvious that it is completely lost in burning and only to a small extent, say one-fifth, regained in coking when by-product ovens are used. In Germany these are almost universal. Here in England the older beehive type, which loses the whole nitrogen, has so far not been completely replaced, and in America up till now the by-product ovens are employed only to a small extent. Though the beehive oven will, without doubt, be universally replaced owing to this saving of fixed nitrogen, the increase of the supply of fixed nitrogen that is to be expected from this substitution will meet the increase in demand only for a very short time. These circumstances afford a tremendous stimulus to chemistry in its efforts to fix nitrogen, of which we have a limitless supply in the atmosphere. Elementary nitrogen is everywhere at our disposal. Its separation from oxygen is brought about by various methods which cost only something like  $\frac{1}{4}$  cent per lb. Against that, fixed nitrogen in the form of Chile saltpetre or ammonium sulfate from the by-product coke ovens has a value of more than 1.6 cents per lb. This price gives a very high working margin and makes possible and practicable quite a number of chemical fixation processes. Now, this is not the first time chemists have tackled this question. When Solvay's soda process came with its demand for ammonia Ludwig Mond attempted to solve the question. He took the lines suggested by Bunsen and Playfair and followed in the steps of Margueritte and Sourdeval, by heating together coal, nitrogen, and barium carbonate for the production of cyanide which can be decomposed into ammonia. But Mond gave up this process after a detailed study. He returned to the supply of fixed nitrogen in the coal, and increased the yield to 70 per cent by the introduction of what is known now as the Mond gas process. This process is continually spreading, as a market is found for the gas of low calorific value which is the other product of the process. In view of this development we may ask what modern aids allow us to carry through with success the task abandoned by Mond and to find satisfactory methods for the fixation of atmospheric nitrogen on a large scale. The answer is obvious if we consider the various processes which have lately been introduced into the technical world.

#### PROCESS FOR OXIDATION OF NITROGEN

First of all, we must mention processes which make use of electric energy on a large scale. The first process imitates the example of nature which produces nitrous products in the track of lightning from the nitrogen and oxygen of the air, by producing a high tension arc in a closed vessel through which air is passed. The foundation of this ingenious method has been laid here in England. Cavendish was the first to get nitrous products from air by help of the spark. Sir William Crookes recommended the use of the high tension arc. Lord Rayleigh and later on

McDougall and Howles determined the yield under varying conditions. The technical forms which have risen to importance are connected with the names of Birkeland and Eyde, Pauling, and Schönherr. They have in common the conception that the technical process must be based upon the use of large amounts of air and electric energy in one single arc flame, and that this problem can be successfully solved only if the discharge is spread out. For this enlarging of the arc Pauling uses a stream of air moving at a high velocity which is blown against the point where the arc strikes between narrow electrodes. Birkeland and Eyde gain the same effect by a strong magnetic field. Schönherr ingeniously uses a steady column of discharge of many meters length which is produced and kept steady by an ascending whirlwind of air, which surrounds the arc. Factories have been started at different places, on the largest scale in Norway. They rapidly captured the small market for nitrites, but in the large field of nitrates the production has not come up to expectations. The obstacle that hampers this industry is the fact that the production of fixed nitrogen referred to the kilowatt-hour does not exceed 16 grams, and that this small yield is obtained only in the form of gases containing no more than 2.5 per cent of nitric oxide. These unfavorable results are due to the fact that the thermodynamic equilibrium between  $N_2$ ,  $O_2$  and NO has an unfortunate value at all accessible temperatures. The importance of this equilibrium has been pointed out by Muthmann and Hofer, and exact figures for the equilibrium have since been estimated in a very ingenious way by Nernst. The following table gives the percentage amount of nitric oxide which according to him characterizes the equilibrium:

TABLE I—PERCENTAGE OF NO IN EQUILIBRIUM WITH AIR

% NO	° C.
0.1	1230
0.5	1660
1.0	1930
1.5	2140
2.0	2300
3.0	2590
4.0	2840
5.0	3060

It is obvious that even at the temperature of the arc only a small fraction can combine with the oxygen unless we may surpass the thermodynamic equilibrium by direct transformation of electric energy into chemical energy. Now experiments carried out in my laboratory have proved that to be possible with small arcs,<sup>1</sup> but there is not much hope of doing so under technical conditions. The upshot of this is that this electric fixation of nitrogen grows up only at places where exceedingly cheap power is available. This is not the case in the chief industrial countries. Conditions are more favorable in the case of the process of Frank and Caro. They fix 50 grams of  $N_2$  by use of 1 kilowatt-hour, everything included. The electric power is used in this case for the purpose of making  $CaC_2$  from  $CaO$  and coal, the  $CaC_2$  being able, after an initial heating, to form spontaneously the so-called calcium cyanamide. There are 36,000 tons of  $N_2$  fixed yearly by this method. The calcium cyanamide can either be used as a fertilizer, or split up by steam with the production of ammonia.

A similar amount of energy is said to be necessary in the Serpek process, which apparently is not yet commercially working on a large scale. It is based upon the change of aluminium oxide with carbon and nitrogen into aluminium nitride. Electrical energy is here required, as in the processes mentioned before, for the production of the temperature necessary for rapid reaction. Starting from bauxite and treating it according to the well known Bayer process to produce the alumina, the Serpek

<sup>1</sup> See Haber and Koenig, *Zeitschrift für Elektrochemie*, **13** (1907), 725; **14** (1908), 689; **16**, (1910), 789. Holwech und Koenig, *Zeitschrift für Elektrochemie*, **16** (1910), 803.

process may be introduced as the first step with the result that the valuable ammonia is obtained as a by-product.

We see that all these processes owe their success to the use of electric energy. The high tension arc requires an extravagant amount and the two other processes require, though much less, still a considerable amount. On closer inspection we find that this fact is the reflex of the values, which the underlying thermodynamic equilibria possess. In the reaction  $N_2 + O_2 = 2NO$ , the right side of the equation which contains the desired fixed nitrogen is thermodynamically less favored than in the reactions  $Al_2O_3 + 6C + N_2 = 2AlN + 6CO$ ; and  $CaO + 3C = CaC_2 + CO$ ;  $CaC_2 + N_2 = CaCN_2 + C$ . But in all three cases the reaction would, in virtue of its thermodynamical properties, never proceed spontaneously at low temperature. High temperature produces the chemical forces required.

In consequence of that, electric energy can be replaced theoretically by other means of obtaining high temperatures. That is the reason why the question of application of flames comes in for the production of nitric oxide from air. But it is clear that the values of the equilibrium between  $N_2$ ,  $O_2$  and  $NO$  which are so unfavorable even at the temperature of the arc will be a still greater obstacle at the lower temperatures of flames and explosions. The subject has been studied for some time in my laboratory. To give an example we arrived at one molecule of  $NO$  with production of 16 molecules of carbonic acid from carbon monoxide. But such results are obtainable only by a large use of the comparatively expensive oxygen to enrich the air and increase the combustion temperature.

Certainly there are enough examples of chemical processes which work successfully on a large scale in spite of the fact that the chemical forces under ordinary conditions are striving to produce the reverse change, from the final products back to the raw materials. The ammonia soda process is an outstanding example. It produces calcium chloride and soda which if simply brought in contact would return to the original form of sodium chloride and calcium carbonate. But in general those reactions are more easily converted into technical processes which are backed by chemical forces tending to change the raw materials into the desired products.

#### SYNTHESIS OF AMMONIA

This consideration led our attention some years ago to the reaction of nitrogen and hydrogen to form ammonia. The heat of combination has, according to thermo-chemistry, a positive value, which proves that it is only due to lack of reaction velocity that the gases do not unite at ordinary temperature. It is true that these favorable values of chemical forces become most unfavorable with increasing temperature. It does not need a very high temperature to make the thermodynamical value of the equilibrium a marked hindrance for any appreciable production of ammonia from its elements. Theory teaches us and experiment has proved that the best mixture of  $N_2$  and  $H_2$  for the production of  $NH_3$  has the value of 1 : 3. But with this most favorable mixture the limit of percentage of  $NH_3$  attainable under ordinary pressure is at higher temperatures very small, as will be seen from the first column of this table:

TABLE II—PERCENTAGE AMOUNT OF  $NH_3$  IN THE EQUILIBRIUM OF THE REACTION  $N_2 + 3H_2 = 2NH_3$

Pressure in atmospheres	Temperature ° C.				
	550	650	750	850	950
1	0.0769	0.0321	0.0159	0.0089	0.0055
100	6.70	3.02	1.54	0.874	0.542
200	11.9	5.71	2.99	1.68	1.07

Especially as the temperature approaches the value of  $1000^\circ$ , for which we easily found effective catalysts, the yield is minute. Some hundred degrees below, the much larger though still small amounts given in the table were formerly inaccessible because of the lack of catalysts effective in the neighborhood of  $500^\circ$ .

At first sight one might think that the thermodynamic situation is still worse for the synthesis of ammonia than for the combination of  $N_2$  and  $O_2$ , because the values of the equilibrium content of  $NH_3$  are much smaller than those for the equilibrium content of  $NO$  in air given before. But theory shows a way out of this difficulty in the case of ammonia which is not open in the other case. The  $NO$  equilibrium is independent of pressure because the number of molecules is the same on both sides of the equation. In the case of ammonia, however, the number of molecules decreases from 4 to 2,



and therefore according to thermodynamics the attainable percentage of  $NH_3$  in equilibrium is proportional to the working pressure over a wide range. Consequently the values of the equilibrium percentage at 100 or 200 atmospheres pressure show a very different aspect, as will be seen from the second and third columns of the table.

It is obvious that technical synthesis is possible if we can succeed in reaching the equilibrium at such pressure and in a short enough time. The current of  $N_2$  and  $H_2$  must circulate in such a way that the ammonia formed by the passage over the catalyst is removed by absorption or cooling before it again passes, mixed with fresh supply of reacting gases. This is the method that was carried through first on a small scale and is now being applied on a large scale. It was necessary to become familiar with the technique of reaction in flowing gases at high pressures. Then catalysts had to be found and studied. The task was somewhat troublesome and I cannot emphasize enough the valuable aid of my countryman Robert Le Rossignol, who was working with me on this question.<sup>1</sup> Earlier experiments had given us the idea that the elements of best catalytic power for producing ammonia from the gases are akin to our first catalysts manganese, iron, chromium and nickel. Thus we tried the metals of the three last groups of the periodic system till we hit upon osmium and uranium. The osmium proved very effective, if used in a very finely divided state, which is easier obtained by heating osmyl-diamine chloride. The uranium is advantageously used in the form of carbide which in the current of nitrogen and hydrogen changes into nitride which forms a very highly catalytic powder. With these contact substances it was found possible to work in the temperature region of  $500^\circ$  to  $600^\circ$  at high pressures, so that the equilibrium was nearly maintained with a high rate of flow of the gas. The very high pressure limits the space which may be filled with the catalyst, but more than 1 kg. of ammonia is easily produced per hour for each liter of catalyzer space. The reaction itself produces the necessary heat because 13,000 calories are set free in this range of temperature by the formation of 1 gram equivalent of ammonia from the elements. The Badische Anilin and Soda Company have taken over and further developed our results. Starting from the observation that contaminations in certain cases increase the catalytic activity in such heterogeneous reactions, they have been able to raise the activity of poorer catalysts to that of osmium and uranium. The result was obtained only after a careful study of the influence of small impurities, some of which are useful while others, even when present in the smallest traces, act as poisons. They overcame certain difficulties in the construction of high-pressure furnaces which became apparent by prolonged working. They developed the purification methods for the hydrogen which became necessary with the replacement of our electrolytic gas by the impure hydrogen from coal. It seems that the task of managing the process on the largest scale has now been carried through satisfactorily.

Reviewing the whole question of the fixation of nitrogen from an economic standpoint, stress must be laid upon the fact that

<sup>1</sup> See Haber and Le Rossignol, *Zeitschrift für Elektrochemie*, **14**, 181, 513, 688; **19**, 53; *Ber. d. chem. Ges.*, **40**, 2146.



there is no reason why all these processes mentioned should not flourish at the same time. The demand is so large that all the efforts in the different directions will certainly not meet it for some time. Considering the subject from the technical point of view the progress compared with Mond's result is obviously due to the introduction of high temperatures and high pressures: *i. e.*, new physical aids. But looking into the matter from the general standpoint we recognize that the thermodynamic equilibrium questions play the deciding part. Theoretical consideration never replaces experiments, but points out and circumscribes the field in which experiment will probably be fruitful.

There is still a large field to be covered by applied inorganic chemistry, and I trust that the combination of experimental skill in chemical work with physical thinking will lead technical chemists to great results.

### CONSERVATION OF NATURAL RESOURCES IN RELATION TO BUSINESS<sup>1</sup>

By JOHN J. MILLER

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That the utilization of our natural resources is of vital importance to the people and especially to the chemists of this country no one will question; that the continued prosperity of our chemical industries is dependent upon an early and proper settlement of this problem is admitted by many, but when the method of simultaneously conserving and using our resources without upsetting business is under consideration, agreement upon any proposition seems difficult. The reason for this state of affairs is, we believe, that the logical, scientific or natural plan of conservation and use has not received due attention. As chemists it is our belief that problems of this kind as well as those in natural science are never solved unless the theory of their solution is in harmony with natural law, and, therefore, we propose in this paper to study the subject from that standpoint, first to refer to the law involved and then to build upon it.

In our opinion, the law pertinent to our proposition is: there are naturally two distinct kinds of business, public and private; private business should be owned by the public, whereas private business should be owned by individuals. This is a very simple and almost axiomatic statement and yet it signifies but little unless we explain that by public business is meant enterprises which involve a franchise, a "right of way" or a natural monopoly. All other business is private. Railroads involve rights of way; telephones or telegraphs require franchises; water power control and timber, coal, ore and oil privileges are natural monopolies.

In the conduct of private business let us say as far as this discussion is concerned that competition should reign. It seems natural that this should be so and whatever is natural is best. As against the argument that competition is extremely wasteful, we venture the suggestion that competition has not, in our time, had a fair trial. As we shall show later, much of our industrial wastefulness is due to too much monopoly rather than to a lack of it.

To decide what policy should prevail in the execution of public business (the question in hand) let us proceed negatively, *i. e.*, by casting aside the less desirable propositions.

1. Is private ownership and operation of public business (especially utilization of natural resources) desirable? Experience up to the present time answers emphatically "No." The socialist movement and the existence of the Conservation League are evidences of dissatisfaction with the system now in vogue, which is none other than private ownership and operation. This method means exploitation of the masses by the few and criminal waste of our natural resources.

<sup>1</sup> This article is an application of the fundamental principles set forth by Henry George in his "Progress and Poverty" and "Our Land and Land Policy."

II. The failure of the existing policy relative to public business has led to government control of private ownership and according to Prof. Van Hise, of the University of Wisconsin, this plan (which he broadens by including private coöperation under government control) will eliminate our difficulties [THIS JOURNAL, 5 (1913), 946-7]. To test this proposition let us turn to the work of the Interstate Commerce Commission, which has for some time controlled the railroads and recently the express companies. In some particulars the people have been satisfied, but without fear of being successfully accused of pessimism we will state that there has been considerable trouble. Little differences of opinion as to wages have been amicably settled, but the question of freight rates is becoming serious. Thousands of men were turned out of the railroad repair shops this winter because the roads could not pay dividends and keep up repairs too. Such conditions are intolerable and inexcusable, but we doubt if a rise in freight rates is the remedy. Everyone knows that the railroads are overloaded with watered stock on which dividends are being paid and it would seem only fair that the governing commission should squeeze the water out of such stocks rather than allow repair shops to close and freight rates to rise. This Interstate Commerce Commission has done wonderful work, perhaps all that is possible under the power delegated to it, but in our opinion the dispensation of justice by commissions is bound to be slow, artificial and cumbersome.

Prof. Van Hise's coöperation feature of the "government control plan" has not been published in detail as far as we have been able to learn but his article in THIS JOURNAL, 5, 946-7, indicates that in the case of coal mining and selling he would divide the country into sections and furnish coal for any given section only from the mines in the same district. This would, he says, destroy the wasteful competition in the various sections. With the government controlling coal prices and freight rates, we may fairly conclude that this system will furnish the consumer his coal at moderate cost whereas he is now paying abnormally high prices, but he will have to use the coal from his section whether it is the kind best suited to his needs or not. If he really wants the coal from his section he would be buying it now and there would be no use of imposing the divisions upon the country. If he is not now obtaining the coal produced in his own section it is because it is more economical for him to use another kind and any restrictions of his buying field would involve a greater loss than at present. We venture the idea that the coöperation which travels hand in hand with unfettered competition is the kind to be sought and the type that will exist when privilege in business is destroyed. Coöperation which is not natural is not desirable.

III. Some may conclude at once that public ownership and operation is the best plan, but we beg to dispense with this idea briefly by saying that if there is a better plan of action, government operation should be avoided because of the danger of political control. It has the advantage, however, of being more in accord with natural law than any method yet discussed.

IV. A résumé of the article at this point will show that we would discard (1) private ownership and operation, (2) private ownership under government control and (3) government ownership and operation. One other combination of these two factors remains, namely, government ownership and private operation.

If this can be brought about, we are in exact accord with natural law, to wit: government ownership of all monopolies and private ownership of business where no monopoly is involved. For example, the common ownership of natural resources signifies the impossibility of private monopoly. In mining by private enterprise (and with private tools) of the natural resources (owned by the government) there is no natural monopoly and, therefore, the operating feature may well be

classed as a private business. This plan then is in harmony with natural law, but let us see if it has any other support.

The purpose of the National Conservation Association is to see that "the minerals should be so used as to prolong their utility. . . . Monopoly of the sources of national wealth should not be tolerated, etc." The methods to be used by this Association are: (1) "Protection of source waters of navigable streams through purchase or control; (2) separation for purposes of taxation of the timber from the land on which it grows; (3) incorporation in all future water power grants by State or Nation of adequate provision for prompt development on pain of forfeiture: payment of reasonable compensation periodically re-adjusted, limitation of the grant to 50 years and recognition of the rights of public authorities to regulate rates of service; (4) legislation whereby title to the surface of public lands and to the minerals therein shall be granted separately and retention by the government of title to all public lands still publicly owned which contain phosphate rock, coal, oil or natural gas and their development by private enterprise under terms that will prevent extortion or waste."

It is evident that our scheme is in agreement with the foregoing, but we should ask ourselves if it is practicable and what is the machinery of its operation. In practice our plan is carried into operation by:

(A) Granting titles to the land surface and the deposits separately. The mining of the deposits would not greatly interfere with the best use of the surface.

(B) Removing taxes from all products of the mines or of timber lands. This will lower the price to the individual consumer and to all industries in which nature's products are used. In the case of timber, which can be replaced, it will augment tree planting and culture. It seems foolish to complain of the destruction of forests and water sheds when we penalize the growing of trees and encourage their destruction by taxing all that remain standing. When we tax oil, which has been taken from the ground, whether crude or refined, we raise its price, discourage the manufacture and sale of oil-using machinery, and burden the industries dependent upon oil.

(C) Taxing ground values or deposit values at the rental rate and equalizing the taxes on used and unused deposits are the last requirements of the proposed system. On first thought this may not seem to be in entire agreement with our natural plan of government ownership and private operation, but we contend that it is in effect identical. The advantage in government ownership of natural resources lies in the preclusion of their monopoly by individuals and this will be attained by taxing used and unused deposits at the same rate. Owners who are now holding out of use these valuable deposits, would use them or sell them to some one who would. This plan is simplicity itself, it involves no coercion or disputes and requires no machinery for its fulfillment other than the machinery of taxation which is already in existence.

But what will be the effect of this system upon our resources and upon business? These are the points in which we are especially interested. Starting with the timber, it is easily comprehended that if timber lands and barren timber lands which are especially suited to timber and are of equal value, are taxed at the same rate it will not be profitable for the owner of the unused land to leave it idle. He will either grow timber upon it or will sell it to some one who will. Can you imagine a better stimulant for replenishing our forests, preventing erosion and loss of soil fertility, and furnishing a supply near at home for our saw and paper mills and other wood product industries? Surely we have no right to complain about the failure of the Almighty to furnish us with necessary wood when we as a people are doing all we can to destroy existing wood and to prevent the growth of more. A simple change in our tax laws will produce timber in exact accordance with the demand for it.

In the investigation of our water power possibilities, which are many indeed and apparently everlasting if we protect our forests, taxation of the monopoly value of these sites whether used or unused would throw them all into use. This would mean competition between the men or companies controlling these water power privileges and consequent minimum prices to the public for the products manufactured. Such conditions are ideal and naturally follow when special privilege is destroyed and freedom of opportunity established.

The effect upon the coal industry and coal resources, of this taxation of title privilege, would be about the reverse of the tendency under the present system of tenure and operation. Now, immense tracts of coal lands are held out of use; only a small fraction of our coal is being mined and that part is sold at exorbitant prices to pay dividends on stock, the value of which depends not upon the amount of product that is mined or sold but upon the monopoly value of the total coal deposits. There is practically no competition between coal companies and what little does exist is between companies which are all overloaded with watered dividend-paying stock. Therefore, the price of coal is high and the chemical industries suffer. Incumbent upon us also is the fact that the operator is hardly ever the owner and the former pays so much a ton royalty to the latter. The operator is interested, therefore, not in taking out all the useful coal but in getting the highest-priced product in the shortest possible time. Is it any wonder that the Bureau of Mines complains about the wastefulness of the present system? Now, this "ground-value-taxation method" of ownership and operation would make it useless for anyone to own coal property unless he was also the user. Moreover, since he would be taxed on his entire holdings, he would be tempted to remove all coal for which there would be a sale.

But lest some one too hastily conclude that all our coal deposits would be mined at once and the supply exhausted, we wish to call attention to the handwriting upon the wall, which reads: "If you will properly utilize your water power possibilities you will need coal only where it is especially adapted and is of greater advantage than water power." Again it is likely that before our coal has entirely disappeared we shall be manufacturing coal out of cellulose or using the sun as a source of power. At any rate we must not overlook the fact that the supply of coal will depend upon the demand. No one is going to mine coal unless the market price insures him a better profit than he can obtain in some other kind of business. As long as there is a demand it will be mined and in several hundred years the supply may be depleted but we should not worry either for ourselves or for our descendants because if we do not waste our coal in mining it and supply only what the public demands (ends which the proposed system will attain) we are within our moral rights, as stated so admirably by Thomas Jefferson when he said: "The world belongs in usufruct to the living."

The ore, oil and other problems are exactly parallel with that of coal. Perhaps no small part of our waste of valuable raw material is due to lack of technical knowledge, want of methods yet undiscovered and the inadequacy of national protective legislation, but economic maladjustments are largely responsible. As long as our resources are privately monopolized they will be sublet at the highest possible rates to operators who will attempt to work them (on a royalty basis) no matter how inadequate their equipment may be. These tenants naturally strive to recover the best, not the most, product in a certain time and at a given cost. Another unfavorable feature of the present monopoly and subletting system is the tendency to operate on too small a scale. What are the causes of this tendency? They must be either lack of capital (perhaps due to too high royalties, taxes on equipment and investment of much money in monopoly enterprises) or difficulty of access to more

raw material (because of private monopolization) or both. The proposed system of equalizing the tax on used or unused resources will make access to larger tracts much easier and the elimination of taxes on equipment and destruction of monopoly will augment available capital. The first step then toward conservation is that of industrial freedom.

Since this paper is little more than an outline, a summary is hardly needed. We desire in closing merely to emphasize the tremendous importance of developing our timber and water power possibilities in order to save our fuel, to ask acceptance of the proposed plan only in so far as it is in harmony with economic law, and to suggest that legislative action relative to the nation's resources should not be artificial, for says the great philosopher and slave, Epictetus, "except in conformity with nature there is no progress."

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### SOCIOLOGICAL WORK OF THE NEW JERSEY ZINC COMPANY<sup>1</sup>

By FLORENCE HUGHES<sup>2</sup>

There has been no stage in the growth of the world that has not brought to mankind its problems. To those of us who are here tonight there is probably no more vital problem than the one of adjustment between the industrial and social worlds. This problem is fast becoming the keynote of prosperity or non-prosperity throughout the civilized nations.

The greatest men of every nation have been those who have offered the best solution to the problems of their day. For this reason it is a most hopeful sign that the men who lead in the control of the great industries of the world are now turning their minds to the solution of the difficulties presented by the two factors—man as a social, human being, and man as a part of the great industrial machine—two factors which were a short time ago so widely separated.

It is through the consideration of this new adjustment that we now find the terms "Sociological Work," "Safety Devices," "Experimental Department," and "Department of Sanitation and Accident Improvement." These terms were not to be found in the business vocabulary of a quarter of a century ago.

To Americans great changes have come in comparatively few years. The great inrush of immigrants, the overcrowding in the cities and the development of large industrial centers have produced conditions which make the need for inter-dependence and cooperation more necessary to the prosperity of this country than in any other nation. If we take the question of our industrial centers, we find much the same conditions existing among the laborers and their families, whether the center be in the city, town or country. Almost without exception we find the immigrant bearing the brunt of the hardest labor. His lack of training, his inexperience regarding conditions of living, his limitation of language and his usually enduring physique relegate him to the rank of the minimum wage earner. The immigrant laborer in our industries is handicapped not only by these limitations, but oftentimes is up against the race prejudice of a boss who underrates his value to labor. This boss has long been the only mediator between the foreigner and the corporation. From this have arisen many of the serious labor problems of the day, and at this point the task of adjustment begins, a task that can be accomplished only through welfare work. I shall not go further into the wider aspects of welfare work, but shall take up the development work that has been carried out by the New Jersey Zinc Company at their various plants.

The first work to be put on a definitely organized basis was begun at Palmerton, Pennsylvania. When the New Jersey Zinc Company built its first plant at Palmerton, about fifteen

years ago, there was only a small group of farms. The next seven or eight years saw the growth of the town to two thousand inhabitants, and in 1907 it had many attractive homes, a park, electric lights, a modern sewage system, bank, hospital, and several churches. These improvements were provided by the Zinc Company in view of the future, and anticipating the time when the town would become a borough. With so much that was outwardly attractive at this time (1907) there was practically nothing being done to meet the needs of the physical, mental and moral welfare of the people. The population of the town was made up of Pennsylvania Germans, Hungarians and Slavs, three elements having nothing in common with each other. The schools at that time were scattered and poorly housed. The churches were each doing a share of Sunday work, but in between times there was nothing being done for the general welfare of the people. There was nothing offered to bring together the various elements among the people and provide them with a common interest. The ever-present activities of the young people were not being utilized. There was nothing being done to stimulate mental activities along uplifting lines or to establish any civic or community spirit in this fast growing town made up almost entirely of strangers brought together from many different points. It was at this time, when, confronted by the barrenness of possibilities of life, that the company decided that corporation responsibility toward the human beings in their charge warranted the establishment and support of an institution that would offer fuller opportunities to the working men and their families. On the well proven ground that a well-trained, right-thinking, contented human being makes a well-trained and intelligent workman, plans were made for the development of Settlement House work.

Two small dwelling houses which were being built in July, 1907, were connected and furnished for use as a Neighborhood House. What was a Neighborhood House? What was the house to be used for? These questions aroused much speculation. Only two answers could be given to start with.

Palmerton was to have a Kindergarten—the first in Carbon County—and the teachers were to live in the house and to form a Home Center, to which all who were willing to come would be welcome at any time of the day or evening. Beyond that, time must indicate the lines of development. The school children indicated the next step and came in increasing numbers, until it was necessary to reckon upon their regular attendance, and thus afternoon classes were formed. Games and stories were so new and interesting that they filled all needs up to Christmas time. After the holiday festivities were over, the need for organized work presented itself and classes were formed in various kinds of handwork.

As the summer season drew near, a new and urgent need presented itself. A public playground, where children and adults could gather for play. The streets of the town were graded above the level of the vacant lots, so there was no suitable spot to be found where people could gather for recreation. It was evident that a public playground would be of good service and one was promptly and generously provided.

The steady growth of the town and the consequent increase of numbers in the attendance at the Neighborhood House, made it necessary, if the settlement work was to develop, to build a new house, and enlarge both equipment and space. This was done and the new house opened in May, 1911.

The kindergarten is used not only for kindergarten class, which has enrolled eighty children between 4 and 6 years of age, but is used in the afternoons for dancing and folk-dancing classes and club meetings; in the evenings for dancing classes, handwork classes and classes for foreigners' English. We have this winter a class of eighty adult foreigners—men and women. These foreigners are being taught practical English. First the necessary human intercourse; then the language which will help

<sup>1</sup> Presented at the 6th annual meeting of the American Institute of Chemical Engineers, The Chemists' Club, New York, December 10-13, 1913.

<sup>2</sup> Superintendent of the Palmerton Neighborhood House.



them in their work. This includes technical terms which they need to know, and lessons in connection with the safety and first aid work being carried on at the plant. They are also taught, through their English, the advisability and possibility of owning their own homes, and the building, buying and selling of the homes as offered by the company is made a part of their English lessons. The work is carried on by a trained worker, assisted by volunteer help of young college men from the plant.

We have in the library about 1600 books for free distribution, among them a good collection of Hungarian and Slavish books; also about twenty popular magazines are on the tables for reading.

The gymnasium is one of the most popular and the most overworked rooms in the house. It not only serves for gymnasium classes and basketball games, but public entertainments and public meetings. One of the most valuable uses of the gymnasium and of the Neighborhood House, in fact, is the Saturday night Open House, which was instituted in a small way in the old Neighborhood House. Every Saturday night, without fail, the house is open to the public for general recreational purposes; there is something for all ages—the children play in the kindergarten room, the girls use the club rooms, those who wish to read use the library, the boys and men use the game room and the bowling alleys, and the young people use the gymnasium for dancing. All available seats are crowded with other members of families, who have gathered to watch the dancing. There is an attendance each Saturday night ranging from three hundred to six hundred people of all ages; this means that up to the present, with a population of six thousand people of various nationalities, Palmerton has thus far escaped the evils of a commercial dance hall, and it is not probable that one, even if opened, would prove a great success in the near future, for the taste for clean, healthy, protected amusement has been cultivated.

The carpenter shop is used not only for boys' manual training work, but also for band practice. We have two bands—one town band, made up of working men at the plant, and the other a Slavish band, made up entirely of foreigners.

Our boys have a cooking class. It has proven one of the most popular and successful of our classes. We have over one hundred school girls enrolled in the different cooking classes, and classes for working girls and older women are held every evening.

In addition to these activities we have carried on, under the auspices of the Neighborhood House, a sewing class for children with an enrollment of one hundred girls, dress-making, lace-making and basketry classes for older girls and women. We have also a banking system, known as the Penny Provident Bank, whose headquarters are here in New York. The deposits from the kindergarten children alone have been over four hundred dollars a year. This money is deposited in a national bank and kept for the children until needed by the parents, and we find it is generally withdrawn for some useful purpose, such as new shoes, clothes, etc., instead of being wasted, penny by penny, on candy and the "movies." We have also a large organization for boys between twelve and twenty years of age, known as the Junior Cooperative Association.

These boys are aiming to follow the pace in civic work, which is set for them by the Men's Cooperative Association—a town organization which holds its meetings monthly at the Neighborhood House. For the girls we have a number of Camp Fire Girls' Circles.

During the past year we entirely outgrew the possibilities of the present Neighborhood House—especially at the kindergarten end. The schools were put in condition financially to assume the burden of a kindergarten, and the company decided to provide a place for another kindergarten. To this end, a small house was taken in another section of the town. This house has been equipped with a kindergarten, which is now enrolled

to its limit of sixty, fifty-five of whom are foreign children. On the second floor of this house there are two rooms which have been furnished as club rooms for men. Owing to the location of the house in the immediate vicinity of the foreigners' homes, it has been adopted by the foreigners and they meet there daily in large numbers and absolute freedom, to smoke, play cards and other games, and to enjoy the music of a Victrola. The latest need of the Palmerton work is for a trained nurse, who will do district visiting in cooperation with the Neighborhood House and the Hygiene Department. A room has been provided for her in the new building, and as soon as the right person is available for the work, which we hope will be in the near future, we shall have a district nurse visiting as a regular part of the Palmerton work.

This covers briefly one phase of the welfare work of Palmerton. There are two other phases which are included in the company's policy—the Safety and Hygiene Departments. Their work is too comprehensive for me to do more than to point the facts, which will show consistent efforts towards welfare and efficiency throughout the organization. From the start, fifteen years ago, the question of safety of employees and the conditions under which they work were carefully considered. In 1911, an active campaign in the interest of Safety First was organized. A committee chosen chiefly from the heads of departments was appointed; an inspector, whose entire time was devoted to this work, were selected to report to this committee. All accidents were carefully investigated and suggestions made for prevention. After the safety work was well established and all practicable safeguards installed, the first committee retired and another in their place was appointed, a Workmen's Safety Committee, under the permanent chairmanship of the Safety Inspector. Experience has proven that the most important work to be done along safety lines is not in guarding machinery alone, but rather in educating employees to the importance of "Safety First" in their work. It is this feature of the work which makes the Workmen's Committee of so much importance. This committee devotes one day each week to safety work.

In the hygiene department we have at each plant of the company an official surgeon, whose duty it is to take care of any occupational diseases or accidents occurring at the plant, all expenses of which are defrayed by the company. At two of the plants (Palmerton and Franklin) hospitals have been established.

In addition to these we have established at all the plants a central emergency hospital, with dressing stations in the various departments. The Safety Committee at each plant has been instructed in the First Aid Work and the committee being large each department has one or more representatives.

All accident cases are referred from the department dressing station to the central emergency hospital and from there, regardless of the severity of the case, to the hospital or to the company surgeon, should he not be in the plant at the time. The surgeon at each of the plants makes a monthly tour of inspection of the plant and reports as to its sanitary condition. In states requiring it, or wherever leaved ore is used, monthly inspection of men exposed to toxic substances is made, and should evidences of poisoning be found the men are transferred to other departments, where they will not come in contact with toxic material. Every accident, occupational disease or illness of any sort is reported each month to the staff member on hygiene, who, in his report to the General Manager, compiles a percentage statistics table in the hope of stimulating competition between the plants in making the Sanitary and Safety Committees more active, and thereby reducing the percentage of accidents and diseases.

The most direct outgrowth of the sociological work at the Palmerton plant has been in the work organized at Franklin, New Jersey, the center of the company's mining interests. At Franklin the same advanced efforts are being made along

hygienic and safety lines as at the other plants, but the same general conditions exist in the life of the working people as were found in Palmerton in 1907, with the exception that the public schools of New Jersey are better than those of Pennsylvania and, therefore, the children of the town are better off than they were at Palmerton. Last summer the company sent the school principal and two members of the school board to Gary, Ill., with the prospect of the possibility of cooperating with the school board in developing work in the school along the Gary lines. Sociological work was begun in a small way last summer by the school principal who organized sixty-three of the boys into the "Borough Boys' Improvement Association."

Efforts were made by and through the boys toward keeping the streets of the town clean. A pond at Franklin made it possible to have a swimming pool. It was necessary first to have it drained and cleaned; this was done and two bath houses built. As much of this work as possible was done by the boys.

The company gave the town an athletic field of five acres. This field has a baseball diamond and a grandstand.

A rifle club was also formed.

After investigation and consideration the company decided to organize at Franklin a Neighborhood House on the same general principles as the one at Palmerton.

An old store building was chosen, renovated and remodeled. This house was opened last month—November 15th. In it they have a large kindergarten room, reading room and library, offices for district visiting nurse, game room for men and boys on the first floor; a bowling alley in the basement; and on the second floor, living rooms for resident workers and caretaker. The Neighborhood House is working in close connection with the public school, so that one supplements the other, rather than one overlapping the other. The public school transferred its kindergarten to the Neighborhood House, the Neighborhood House providing one teacher and the public school providing the other. The school principal is on the staff of the Neighborhood House workers and five of the public school teachers are resident workers at the Neighborhood House, giving part time service. There are now enrolled eighty children in the kindergarten. The boys are organized into clubs, meeting twice weekly; the men are making constant use of the game room and bowling alleys; camp fire circles for the girls are being formed. As the work at Franklin is barely a month old this is a good beginning and further developments will be controlled by the needs of the situation.

At the Nassau plant at Depue, Illinois, the work has been chiefly, up to the present, along safety and hygienic lines. A regular physician spends a portion of each day at the plant and is available at all times. In the spring of this year a visiting nurse was engaged and a small emergency hospital built.

This hospital contains an operating room and an office for the nurse, and a room with one bed for the use of a badly injured patient until he can be removed to the hospital at Spring Valley, an adjoining town. In addition to the work at the plant, the visiting nurse visits the public school weekly to examine all the school children. The nurse organized a mothers' club and sewing class and was instrumental in starting the two months' free kindergarten. This latter work was done in view of developing at a later time wider work along purely sociological lines. The Nassau plant has a safety committee, organized with a master mechanic and six workmen as members. A night school has been established in cooperation with the University Extension Department of the State of Wisconsin. There are eighty-five men enrolled in classes to study English, arithmetic, algebra, mechanical drawing and elementary chemistry.

The company is building simple bungalow houses at each of their plants in view of doing away with overcrowded conditions of living and offering the laborers an inexpensive home which they can buy on easy terms from the company.

The work at Austinville, Virginia, has also been chiefly along the line of sanitation and improvement of living conditions. It was aimed, in the beginning, at the bad conditions usually existing in villages not supplied with a sewage system. Through persistent effort and by personal work done with each employee, cooperation was won, until a majority of the houses have been put in as good hygienic condition as is possible under the circumstances. A competition for the improvement of the ground around the houses was inaugurated and prizes varying from \$5 to \$25 were offered. The rules for prizes were as follows:

1. All employees who live in company houses shall be eligible to this competition except salaried employees.

2. Inspections shall be made by a committee composed of the superintendent, doctor, and farm manager once a month from and including May to October, and prizes shall be distributed about November 1, 1913. The first inspection shall be made about May 15, 1913.

3. The award of prizes shall be based upon the result of all the inspections and upon the regular reports of the doctor and the sanitary inspections.

4. The inspections by the committee shall not include the interior of houses, but shall cover the following points:

- (a) Sanitary conditions of premises as relates to condition of out-houses, pig pens, stables, chicken runs, and disposal of garbage.
- (b) Condition and productiveness of vegetable gardens.
- (c) General appearance of premises as to tidiness, improvement by means of flowers, vines, trees, etc.

5. Regularity of attendance at work and relative freedom of each family from the usual summer diseases shall also be considered in making the awards.

So much interest was taken in this improvement work that it was necessary in many cases to suggest moderation; and a surprising degree of interest, taste and skill in gardening was shown by a majority of the people in town.

In conclusion I would say that sociological or welfare work in connection with any corporation should not be gone into as a form of philanthropy, but rather as a good business proposition. With this in mind I would say that in beginning social work in a community I would recommend settlement work for various reasons: *First*, it can and should be begun in a small way, with possibilities of developing along the lines indicated by the needs of the community. No two communities have the same needs. *Second*, work should begin with the children and this work should be educational. Therefore, the kindergarten makes the best starting point, for through it the workers have the closest point of contact with the homes through which the community is to be reached. *Third*, it should have a flexible policy and should be without the limitations of race, creed or sex. This is one of the strongest pleas in favor of settlement work. And lastly, those undertaking it should go into it anticipating its growth and willing to meet the demands of success, which mean, as time goes on, increased equipment and enlarged space. Just to what extent this is to be carried of course depends entirely upon the special situation in which the work is found and the conditions to be met. Welfare work is not intended to offset fair wages. To the credit of those who are doing welfare work it can be said that investigations have proven that corporations who are doing welfare work do not fall below the scale in question of wages. But the wage that is fair to the workman from the point of view of value given to his employer, does not mean to the large mass of laborers a wage that is sufficient to keep his family in more than the necessities of life. It does not mean that he is able to provide anything in the way of education, which the public does not offer him. It does not mean that he can provide suitable recreation for his children and it does not mean that he can provide them with books. Therefore, whatever the laborer and his family are to have above and beyond the necessities of life must,

under present conditions, come entirely from outside sources. Man as a unit is not worth sufficient wage in most cases to give advantages to family and, in far too many cases, would not use money for such purposes when earned. The body of workmen, representing composite labor of an organization, should have, not as chafity, but business justice, the best the company can afford to give them.

If the industry to which the laborer belongs is located where he has access to good schools, public libraries and clean recreation places, the corporations' responsibility is lessened; but it is seldom that large industrial plants are so located that the working men can have these advantages. Therefore, it would seem that the responsibility of providing something above the bare necessities of life is up to the corporation. For in the end, it is from the laborer and to the laborer to whom our great industries have to look for their existence and their prosperity.

Before leaving the question of purely welfare work as separate from any question of safety and sanitary work, which is fast becoming a part of the law, I would like to speak of the question of appreciation. We are often asked by visitors who come to the Neighborhood House, "Do the people appreciate all this?" If by appreciation we mean, "Do they come and present their thanks for that which is being offered them," I would say "very seldom." But if we mean by appreciation, "Do they take advantage of the opportunities offered? Are they glad to come to all the classes and gatherings provided for them? Do they want their children to profit by the opportunities offered?" I would say "Yes." But let us stop and consider that the last human quality developed is the one of appreciation. We appreciate things after they have passed. How many of us appreciated what our homes did for us when we were children? How many of us appreciated what the school and college did for us? How many of us now appreciate what is offered to us in public museums, public libraries? How many of us appreciate what the State and Nation offer us? Therefore, do not let us be too quick to expect the man who needs our help to develop as one of the first qualities this power of appreciation.

Will the corporation get its return for the money invested in welfare work? That is a question which cannot be answered in dollars and cents. It is an output from which the return must come in an intangible form, but we believe that it does come in the form of better workmen, better citizens and more united organizations.

I would like to state that the foregoing has not been offered as what I once heard said at the end of a similar talk, "A very pretty picture show." It stands for something real and something vital. If my words have not been convincing I can only say, "Come and see for yourself what is being done. We have the goods to show."

PALMERTON, PA.

## WELFARE AND SAFETY PROVISIONS AT THE WELSCHACH COMPANY'S PLANTS<sup>1</sup>

By HOWARD LYON

Some seem not to be satisfied with an account of the welfare work of corporations unless they are assured that this activity originates from altruistic motives. It may as well be stated at the outset that welfare effort was partly prompted by statutes and further by considerations of profitable business. However, with the work well under way, we are convinced that humane treatment of employees is as good business for corporations as for individuals employing labor. Forgetting the cold term "corporation," it is well to bear in mind the fact that the affairs of corporations are conducted by real men, men of large heart and red blood, who are keenly alive to sentiments of consideration for co-laborers.

Welfare work now in force with the Welsbach Company has accomplished in large measure the following results:

- First. Safe conditions of labor.
- Second. Fire protection.
- Third. Measures for the health of employees.
- Fourth. An Employees' Relief Association.
- Fifth. Provision for aesthetic and cultural betterment.

It may be seen at a glance that these results, in the order named, are increasingly farther and farther removed from justification by purely business considerations. However, the world's experience has proved that the human machine works efficiently only under the impetus of treatment that is just, kind and considerate.

The Welsbach Company has elected to assume the liability imposed by the New Jersey and Ohio State laws relating to injuries incident to service.

Naturally the company has sought to minimize its money obligation by providing every possible means of avoiding accidents.

Guards, cases, or gratings protect the fingers, arms and clothing from being caught by gears, saws, belts, punch presses, knives and shears. All grinding wheels are encased except at the point of use to safeguard the body or eyes from flying fragments. Buffers in continuous use have the dust exhausted by suction fans, and workers are supplied with face hoods equipped with wet sponges for the nose. Punch presses are provided with means so that they cannot be operated except with the two hands in positions of safety.

Exhaust hoods carry off vapors from noxious acids. Mantles are dried, after collodionizing, in closed chambers from which the heavy vapors of wood alcohol and ether are carried downwards. The eyes are shielded from the intense glare in hardening mantles by plates of blue glass. All stairways, elevator shafts and dangerous passages are guarded by rails. Trenches are guarded by rails and at night by lanterns. Everywhere the notices read that safety appliances must be used, and that guards must not be removed.

When a man prepares to go into a boiler, to clean or inspect it, he draws the fire and closes and locks, in a portable iron case, the outlet steam valve, the inlet hot water valve, the blow-off valve and the flue damper. *He enters the boiler with the locking keys in his own pocket.*

Rubber gloves, aprons, boots and coats are furnished to operators or workmen who might be injured by chemicals or water. Caps are provided if the hair is liable to be caught. Places subject to fire or explosion from combustible gases are lighted with closed lamps.

A Pulmotor is owned by the company and is offered for use to all local physicians free of cost. Quite recently by its use a man outside of our works was saved from death by asphyxiation.

As an illustration of good business involved in provision for safe conditions of labor, and further by a policy of self-insurance, I may state that our liability under the law last year amounted to about \$700. Without our present safety devices and precautions, insurance covering these risks would have amounted to \$2600. We have gained amply by our expenditure and our employees have been able to earn full pay for a larger proportion of their time and possibly even their lives have been saved.

Our company is in sympathy with the liability law. By assuming liability, fees and costs are saved both by the company and the injured party. Both parties fare better under the policy of self-protection than through outside insurance.

A recent accident case will illustrate this point. Some weeks ago a boy slipped from an elevator and was forced back against the walls of the shaft and pretty severely mangled. The company had him removed to a hospital immediately. As the seriousness of his injuries became apparent, he was taken out of the

<sup>1</sup> Presented at the 6th Annual Meeting of the American Institute of Chemical Engineers, The Chemists' Club, New York, December 10-13, 1912.



public ward and put into a private room. One and at times two special nurses were employed to attend him. He was cared for and operated on by a skilled surgeon not of the house staff. Under this treatment the boy has fared splendidly and has now been discharged from the hospital. An insurance company would undoubtedly have left the boy to the tender mercies of the public ward where his chances for life would have been much smaller. This humane treatment of the case meant life to the boy and *actual money saving to the company.*

In its branch factory at Columbus, Ohio, the Welsbach Company insures with the State Liability Board of Awards, because the board is a humanitarian agent and may thus be expected to pursue a humanitarian policy.

All buildings occupied by our company are equipped with automatic sprinklers. A pressure of 80 lbs. is maintained continuously in all mains and branches by two fire pumps. There is ample power to maintain this pressure with hose lines in use. Our system furthermore is connected with a similar system of the adjacent Argo Cotton Mills and with city mains. Hose houses at all important points outside the buildings are supplied with hose, axes, bars, wrenches and extra nozzles. All hydrants are inspected weekly and fire drill is carried out every Saturday afternoon. In case of fire every man knows his place. There are at least two exits from all factory rooms. Fire danger to operatives is small, as the buildings are not of over two stories. A night force of at least ten men is ready for action at a moment's notice. Protection from fire is important not only in the working hours but also at night, for a destructive fire would necessarily deprive employees of their employment and income.

Provision on the part of the company for safeguarding the health of employees is ample and somewhat exceptional in its scope. A limousine and open car are on call constantly to convey any injured or ill person to the hospital or home. This use is the principal object for maintaining cars. We have in our own enclosure a hospital with an attendant trained nurse and all the means for first aid treatment. A salaried physician is in daily attendance and is in duty bound to respond to any call at any time.

Employees whose work subject them to exceptional danger are examined to determine their physical fitness for that work. For instance, where there is danger of injury to the eyes, only those whose eyesight is perfect are engaged for the work. In one respect our provision for the health of employees is unique. Any employee either at the works, at the physician's office or at his own home may get advice, medicine or treatment free of charge. A dispensary at the hospital supplies free of charge medicines for temporary ailments. All accidents are reported at once by the nurse to the superintendent's office.

I have already mentioned the use of exhaust fans for carrying off the vapors in the drying process following collodion dipping. Similar fans are employed to bring cool fresh air into our hardening rooms, as these rooms are subject to excessive temperatures, or vitiated air by the burning off and hardening processes. In these rooms there are also conveyors of fresh and cool air at the machines of individual operators.

Shops and other rooms where the ventilation conditions are more nearly normal are provided with roof or ceiling ventilators.

During the past year an Employees' Relief Association has been formed with a membership of about seven hundred. The treasurer of this organization, a man who has reached mature age in the service of the company, is paid a salary by the company to give his extra attention to collections of fees and disbursement of relief funds. It goes without saying that the company is in no direct way remunerated for this expenditure.

The following table gives the classification of risks as based on earnings and possible benefits in case of sickness or death:

Class	Weekly pay	Weekly fee	Benefits to individuals or their dependents
A. ....	\$5.00 or less	5 c.	\$2.50 per week for 13 weeks, or \$50.00 at death.
B. ....	\$5.00 to \$10.00	10 c.	\$5.00 per week for 13 weeks, or \$75.00 at death.
C. ....	Over \$10.00	15 c.	\$7.50 per week for 13 weeks, or \$100.00 at death.

During the few months that this Association has been in existence, it has paid out in benefits about \$250 and has a balance on hand of about \$1500.

Our company has not confined its welfare activity to watchfulness of the material well-being of employees, but has expended and is constantly expending large sums of money to make the plant attractive to the social and aesthetic sense of its workers. We have large stretches of well kept lawns broken by rare trees and shrubs and beds for a succession of flowers. The artistic gateway, paved driveways, concrete walks, vistas of beautiful grounds and ivied walls give the appearance of a public park rather than a place where human toil is turned to profit. An experienced gardener and one or two assistants are employed continuously in beautifying the grounds.

One attractive building serves the double purpose of hospital and club house for the women employees. It is comfortably and attractively furnished and has a lunch room in the basement where tea, coffee and milk are supplied at 2½ cents per glass or cup. The management of the club house is vested in an organization of women workers. The rooms are open for use during the day and also in the evening by permission conditioned on the presence of some responsible matron. In the latter case young women are privileged to entertain their men friends. A piano bought by the Welsbach Company constitutes a part of the furnishing. For a similar provision at Columbus a piano is rented. There is a weekly meeting of a girls' sewing society in the club house.

The nurse of the hospital adds the refining influence of a rare personality to the experience of the young women. The nurse states that young women are constantly coming to her for counsel.

Something is being considered in the way of providing a similar club house for the male employees, with lunch room and smoking room. A fine tennis court has been laid out for the use of employees during the day or in the evening, and is largely used.

Considerable effort has been made through volunteer instructors to maintain night classes in various subjects, but it is felt that these classes cannot be in a large sense successful without the privilege of attendance on company time and the services of a regularly paid instructor. Such a plan has been considered.

A measure recently put in force is significant and instructive to those who dwell upon problems of efficiency in industrial work. At the middle of the morning and afternoon work periods, 400 or 500 girls and women employed in mantle operations are given a rest period of 5 min. for relaxation and fresh air. This measure means a mathematical loss of service amounting in the aggregate to about \$2000 per year. Experience up to the present time, however, indicates a gain rather than a loss by reason of a fresher spirit for exacting tasks.

Reflecting upon the practical operation of the various measures in force to make our employees more comfortable and happy, we are led irresistibly to the conclusion that if we treat our workers considerably along the lines indicated, we get a full measure of human toil and promote at the same time the well-being of the men and women that render us service. Those who plan and those who toil experience a finer spirit of effort and accomplishment. All other considerations aside, it is the part of wisdom to free the management of a large company from the depression and anxiety fomented by discontented employees

that it may give itself to the larger problems of prosperity and growth. As of old, so it is true here and now: "Give and it shall be given unto you."

I have narrated above the prosy details of our provision for the well-being of our employees. I have shown that these provisions have resulted in gain both to the employees and to the company responsible for them.

I would like to emphasize more fully the value of beautiful and artistic surroundings.

A visitor at the Bethlehem Steel Works, noting the display of bedded plants about the buildings, asked Mr. Schwab whether the establishment was making steel or raising flowers. Mr. Schwab's answer was in substance, that the works were primarily intended for the production of steel, but with beautiful surroundings they were able to make better steel and more of it.

Our observation confirms the correctness of Mr. Schwab's opinion as applied to our own products. Mr. Schwab said further that the workmen were so impressed that they were beautifying their own homes in the same way.

Back of the leather apron or the work-a-day clothing, there is the same fine heart and lively response to every form of expression of beauty possessed by others whose fortune and taste give a larger realization of ideals of loveliness. When the beauty of well-kept grounds greets the workman as he walks toward the machine which he is to operate, there is a little faster beating of the heart and the morning air is breathed a little deeper. Then comes the feeling of pride in work and hope of better days and larger opportunities. And to those who experience this feeling better days *do* come. Best of all the elements of better days is the deep-seated sentiment of appreciation of the finest objects and experiences that life can offer. Light, pure air, clean and artistic surroundings, with attendant good health, are fundamental to growth and attainment.

GLOUCESTER, N. J.

## COTTONSEED FLOUR AS A POSSIBLE FOOD FOR MAN<sup>1</sup>

By C. A. WELLS

One of the earliest reported cases of the use of cottonseed flour as a food for man was that in which bread and other articles of food prepared from cottonseed meal were served certain members of the Farmers' Congress held at College Station, Texas, about fifteen years ago. Since that time a number of reports have been made of the use of the meal in human diets.

Allison<sup>2</sup> states that many of the smaller cottonseed oil mills of the country are manufacturing so-called "cottonseed flour" and that some of the larger mills are producing and disposing of it with profit. It is not manufactured by any secret process, but is simply cottonseed meal of choice color, taste and odor which has been finely ground and thoroughly bolted. As might be expected, therefore, it contains more protein and less crude fiber than cottonseed meal of similar grade and origin. In other respects the chemical composition of the two is essentially the same. The terms "cottonseed flour" and "cottonseed meal" are used synonymously throughout this paper.

Cottonseed flour contains little kneading principle and more than twice as much protein as meat. In order, therefore, to facilitate the making of bread and at the same time reduce the protein content of the latter, the flour is usually mixed with some other substance such as wheat flour. Most of the cottonseed flour bakery products found on the market are prepared in this way.

One does not know the degree of digestibility of cottonseed flour when eaten by man, but from the known digestibility of cottonseed meal for cattle, Fraps<sup>3</sup> concludes that 85 per cent of the fat and protein is digestible for man but believes the nitrogen-free extract to be not so completely digestible. Mendel and

Morris,<sup>1</sup> who recently experimented with dogs, conclude that cottonseed meal is but poorly digested, only 67-75 per cent of the nitrogen in the meal being absorbed as compared to 94 per cent for fresh meat. In addition to its general fitness as a food for man, Hart<sup>2</sup> believes and Moore<sup>3</sup>, Allison<sup>4</sup>, and Thompson<sup>5</sup> state that, owing to its freedom from carbohydrate, it has a specific food value for diabetics.

### FOOD VALUE OF COTTONSEED FLOUR

The total food or energy value of any foodstuff may be conveniently expressed in calories per pound. It will be interesting to note in the following table the high caloric value and low cost of a pound of cottonseed flour as compared to that of a pound of steak, especially as regards protein, which is almost always an expensive constituent of diets. Thus for six cents one can purchase as many protein calories in the form of cottonseed flour as for one dollar in the form of steak.

TABLE I COMPARATIVE ENERGY VALUE AND COST OF STEAK AND COTTONSEED FLOUR

	Fuel value per lb.			Comparative cost of 1000 calories	
	Fat calories	Protein calories	Total calories	Cottonseed flour at 2c.	and steak at 20c. per lb.
Beef- loin.....	517	417	934	\$0.50	\$0.245
Lean beef flank.	458	399	857	0.47	0.215
Cottonseed flour.	517	708	1619	0.028	0.012

### ECONOMIC IMPORTANCE

In 1912 there were crushed in the United States<sup>6</sup> 4,921,073 tons of cottonseed equivalent to about 2,160,000 tons of meal. If we make the reasonable assumption that cottonseed meal has a digestibility of 70, then on the basis of the food values given in the table above, one ton of meal has a protein caloric food value of \$495.60 or a total caloric food value of \$555.37.<sup>7</sup> Until 1898 nearly one-half of the annual production was exported, the remaining half was fed to stock or used in making fertilizers. The Interstate Cottonseed Crushers Association arbitrarily classifies cottonseed meal into three grades: choice, prime and off grades. Choice meal is from choice cottonseed finely ground. It must be perfectly sound, sweet, and of a light yellow color, free from excess of lint and hulls. It might be inferred that meal of this grade would be suitable for human consumption. Unfortunately, however, we have no record of the quantity of each grade of meal manufactured, so that one has no accurate data upon which to base a calculation of the amount of meal even presumably of a grade fit for man's use as a food. On the percentage basis, however, if cottonseed meal can be used as a food for man and if it has a digestibility coefficient of 70 or greater, then 10 per cent of the meal produced annually in the United States (10 per cent of 2,160,000) would have a total caloric food value of \$119,959,920 and a protein value of \$106,920,000 (216,000 multiplied by \$555.37 and \$495.60, respectively). The same meal when fed to stock or used as a fertilizer would have a value not exceeding \$6,480,000 (216,000 × \$30.00, a liberal commercial value of one ton of meal).

### EFFECTS WHEN FED TO MAN

Allison, Thompson, and others state that it is a suitable foodstuff for man and that in many cases its continued use has proven highly beneficial. According to Fraps<sup>8</sup> "we have no reason to believe that cottonseed flour will not be a wholesome food, when used in small amounts to replace meats, or to re-

<sup>1</sup> Mendel and Morris, *J. Biol. Chem.*, **11**, 1-3 and 5-26.

<sup>2,3,4</sup> and <sup>5</sup> Circular Letters.

<sup>6</sup> U. S. Dept. of Com. Bureau of Chem. Rept., 1912.

<sup>7</sup> 708 multiplied by 7000 gives 1,416,000 as the number of protein calories in one ton of meal. 70 per cent of this equals 991,200, the number of digestible calories. This number divided by 1000 and multiplied by 50 (cents) gives \$495.60 as the protein caloric value of one ton of meal.

<sup>8</sup> Loc. cit.

<sup>1</sup> Read at meeting of Section C of the Association for the Advancement of Science, Atlanta, Georgia, January 2, 1914.

<sup>2</sup> Allison, Personal Letter.

<sup>3</sup> Fraps, Texas Agric. Exp. Sta., *Bull.* **128** (1910).

inforce a diet poor in flesh food," yet he says further "we are inclined to believe that the maximum amount of cottonseed meal which should enter into the diet is two to three ounces per day; that the conditions under which such a diet may prove injurious must be established.....and that only experience and experiments can tell us the part which cottonseed flour should play in nutrition and under what conditions it may prove unwholesome." The writer has eaten for some time in his own home cakes and bread of various kinds containing a portion of cottonseed flour without experiencing any ill effects from its use.

It should be said, however, that while there are no reported cases of injury from the use of the meal as a food for man, it is possible and indeed quite probable that this is due to its so far limited use for this purpose. The assumption of its unwholesomeness for man naturally grows out of the well known injurious effects which it produces when fed to stock. Investigations are now under way to ascertain the true nature of cottonseed meal toxicity. If this can be done, cottonseed meal or flour may be given to the world as a new and exceedingly inexpensive food with an almost unlimited source.

CHEMISTRY LABORATORY, GEORGIA EXPERIMENT STATION

## WILLIAM H. NICHOLS MEDAL AWARD

The Nichols Medal was conferred upon Professor M. Gomberg, of the University of Michigan, in recognition of his distinguished researches on triphenylmethyl and its analogues. The medal meeting was held in Rumford Hall, The Chemists' Club Auditorium, on Friday evening, March 6, 1914, with Dr. Allen Rogers, Vice-President of the Section, in the chair. The presentation address was made by Dr. Bernhard C. Hesse. Professor Gomberg, in acknowledgment of the medal, presented an address on "The Existence of Free Radicals," in which he gave the first complete review of his eighteen years' investigations and drew his conclusions based upon the results of his work. A large number of papers representing the stages of these investigations have been published in the *Journal of the Society*, and a complete review of the work to date is now in course of preparation.

Professor Gomberg has prepared an abstract of his address which is published below, together with the presentation address by Dr. Hesse.—[EDITOR]

### PRESENTATION ADDRESS

By BERNHARD C. HESSE!

The purpose of this meeting of the New York Section of the American Chemical Society, is to present the William H. Nichols Medal to the author of what has been determined by the Jury of the William H. Nichols Medal, to be the best original paper contained in the publications of the American Chemical Society during the year 1913.

The purpose of the William H. Nichols medal is the stimulation of research in chemistry.

Research has latterly become a topic with which to conjure. It is regarded by many as a panacea for the disabilities of chemistry, applied and pure. Yet there is no magic in research; no marvels are performed by it. You get out of research precisely what you put into it. You no more get something for nothing in research than in any other effort.

There is, however, a divergence of opinion as to what does constitute research. As I view it, research is the orderly, systematic development of and addition to science; science is nothing more nor less than the orderly, systematic and co-ordinated record of human experience. Purely accidental or random addition to our knowledge without causal connection with what precedes and with what follows, however valuable or beneficial the addition may itself be, is not research. Yet, research is not wholly independent of accident nor of chance; the systematic, orderly and planned exploitation of that which chance or accident may have thrown into the path of him who is engaged in research, together with the carrying out of the original plan brings research to its highest state of efficiency and to its ample justification. Chance, without system, leads to chaos. System, even without chance, leads to an orderly and co-ordinated statement of what we know and of what we know not to be. Negative information, if true, has the same value as positive information.

He who engages in research must have not only a working knowledge of what has gone before, but also a working knowledge of all the tools at his disposal; he must have a creative imagination, so that he may set himself the problem and forecast with greater or less certainty that which may be expected; he must be prepared to deal with and to recognize the unexpected or unforeseen; he must have within himself a sterling quality of rigid self-analysis and a stern judgment of that which is of his own creation. Without a creative imagination, balanced by a knowledge of the uncertainties of hypothesis and of theory and without balance by a knowledge and an appreciation of the imperfections of all human effort, he who engages in research is led into the highways and by-ways of confusion. Research information which is incorrect or confusing and work that leads to it are worse than useless, and he who knowingly produces such results is false not only to himself but to the best and highest traditions and aims of research. Those who engage in research must have a thorough and an abiding desire for truth at all costs and must be satisfied with nothing as true which has not been demonstrated to be true by every test that can be reasonably applied. The more fundamental the nature of that which is believed to be new, the greater the necessity and responsibility for rigid scrutiny and inquiry as to its accuracy. Power of observation without the ability or without the quality of character to scrutinize and test the results of observation as to accuracy and certainty, is useless in research. Successful research requires a happy blending of many of the qualities of those who have explored and made our earth habitable, namely, daring, tempered with caution, and imagination, balanced by judgment.

Those acquainted with the published work of Professor Gomberg, our guest of honor this evening, recognize that his work fulfills and typifies the highest ideals of research. Starting out to obtain an answer to a definite problem in a carefully planned and definite way he came across something new, unexpected and unusual. His patient, laborious and ingenious examination of this led to the work which has consumed much of his time and effort for the past eighteen years and has given to chemistry a new class of substances—triphenylmethyl and its derivatives.

Professor Gomberg, it is my privilege as Chairman of the New York Section of the American Chemical Society now to place in your hands this, the tenth gold impression of the William H. Nichols Medal as a token of the appreciation and esteem in which we hold your work as a chemist and the encouraging example you have thereby given for all who engage in research.

### THE EXISTENCE OF FREE RADICALS

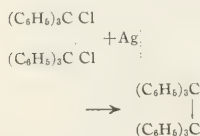
By M. GOMBERG

From the time when Kekulé and Franchimont first prepared triphenylmethane, numerous attempts were made to prepare the analogous compound tetraphenylmethane, but seemingly without success. The assumption was made that this substance

<sup>1</sup> Chairman New York Section of the American Chemical Society



must be very unstable and consequently incapable of existence under ordinary conditions. In 1897, a reaction was worked out by the writer by means of which a hydrocarbon, supposedly tetraphenylmethane, was produced. The compound proved quite stable, melting at 280° C., and distilling undecomposed at 430° C. In order to obtain more evidence as to the constitution of this hydrocarbon an attempt was made to prepare, for comparative study, the next higher completely phenylated analogue, namely, hexaphenylethane. Accordingly triphenylchloromethane was subjected to the action of metals—silver, mercury, zinc, sodium—with the full expectation that the reaction would proceed normally and give rise to hexaphenylethane:



A hydrocarbon possessing the requisite composition (C = 93.8 per cent, H = 6.2 per cent) was actually obtained. But the proneness of this new compound to enter into the most varied chemical reactions, and its strikingly unsaturated character, precluded the natural inference that the compound at hand was actually hexaphenylethane. The opinion was expressed that here was an instance of a compound with one atom of carbon in the trivalent state, *i. e.*, triphenylmethyl,  $(\text{C}_6\text{H}_5)_3\text{C}$ , a free radical. Subsequently it was found that many analogues of triphenylmethyl are capable of existence. In other words, there is a large class of such free radicals—a class of triarylmethyls.

**General Reaction and Method of Preparation**—When a triarylmethyl halide, dissolved in benzene, is treated with some metal in the absence of oxygen, the halogen is taken out by the metal and the unsaturated triarylmethyl is formed.



The solution is invariably colored, the nature of the color depending upon the nature of the three groups in combination with the central carbon atom. The colored compound is extremely sensitive to the oxidizing influence of the air, consequently when the colored solution is exposed to the air, the color disappears. In order to prepare a triarylmethyl pure the essential conditions are: exclusion of moisture—to prevent the hydrolysis of the triarylmethylchloride itself; absence of oxygen—to prevent the oxidation of the resulting unsaturated hydrocar-

bon. A convenient form of an apparatus which assures the above conditions was described by the writer<sup>1</sup> some years ago. It permits of the preparation, recrystallization, filtration, washing and drying the final product without ever exposing it to the oxidizing influence of the air.

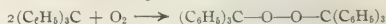
**Physical Properties**—The simple representative, triphenylmethyl itself, is in the solid state undoubtedly colorless, but goes into solution with the production of a distinct orange-yellow color in any solvent whatsoever. We are forced to conclude that the compound in dissolving must undergo a change in molecular structure. To Schmidlin belongs the credit for the proof that even in solution the two modifications, colorless and

colored, exist side by side in equilibrium with each other. In the solid state triphenylmethyl can be kept for years without change. It melts at 145° C.

The unsaturated character of triphenylmethyl is evidenced by its avidity to unite with a variety of solvents, taking them up as solvents of crystallization, and easily losing them at slightly elevated temperatures. It unites with aromatic and aliphatic hydrocarbons, with ethers, aldehydes, esters, ketones, nitriles, carbon disulfide, chloroform, etc. The composition of these various additive products is quite uniform, being  $2(\text{C}_6\text{H}_5)_3\text{C} + 1$  molecule solvent. Another striking characteristic of triphenylmethyl is its capacity to function as an electrolyte. When dissolved in liquid sulfur dioxide, a very good ionizing solvent, it conducts the electric current well, and its molecular conductivity increases with dilution.

**Chemical Properties**—Foremost among the chemical reactions of triphenylmethyl and all its analogues is the readiness with which they unite with oxygen. Triphenyl-

methyl in benzene takes up oxygen from the air at the rate of 60 cc. in one minute for 1 gram of the hydrocarbon. The compound formed in this reaction is colorless, fairly stable, and has the constitution of a peroxide:



As these peroxides are but little soluble in the usual organic solvents their purification presents no difficulties. Consequently the isolation of a peroxide in a reaction as described, is sufficient proof that a compound containing a trivalent carbon atom is present.

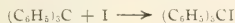
Next to the combination with oxygen, the behavior of tri-

<sup>1</sup> *Ber.*, 37 (1904), 2033.

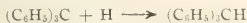


M. GOMBERG, WILLIAM H. NICHOLS MEDALIST, 1914

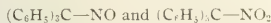
phenylmethyl towards halogens is very striking. It unites instantly with iodine, even in very dilute solutions, giving almost quantitatively triphenylmethyl iodide:



Triphenylmethyl also combines with hydrogen in the presence of finely divided platinum:



It also adds on nitrogen oxide as well as nitrogen dioxide, giving nitroso and nitro-triphenylmethane:



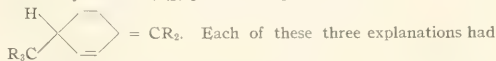
In addition to all the various additive reactions it also reacts with phenols, amines, and hydrocarbons, giving tetraphenylmethane derivatives, and is readily affected by light, suffering auto-oxidation.

*Constitution, First Period, 1900-1905*—It is obvious that the entire chemical behavior of triphenylmethyl finds its most consistent and most plausible explanation in the hypothesis that this hydrocarbon is a free radical containing a trivalent carbon atom. This explanation when first advanced was received without open opposition, but none the less with hesitancy. The hesitation to acquiesce in the hypothesis of the trivalency of carbon received later its main support from the fact that the molecular weight of triphenylmethyl was found to be not 243, but double that. Here then was the dilemma: The chemical behavior of the unsaturated hydrocarbon speaks forcibly, almost exclusively, in favor of the trivalency of carbon. The only argument against this interpretation is the dimolecular state of the compound, one single physical constant. It did not seem, however, impossible to reconcile this apparent contradiction between the molecular weight on the one hand and the entire chemical behavior of the compound on the other hand. We have numerous examples among inorganic as well as organic compounds where substances in solution possess abnormally high molecular weights, double and triple that demanded by the composition and constitution of the compounds in question. We say under such circumstances that the compound exists in the associated state, *i. e.*, several molecules unite to form a single aggregate. Is not water itself poly-molecular, the size of the aggregate varying with the temperature? Are not the organic nitriles, the acids, the acid-amines, di- or poly-molecular in solution? To quote from a paper of ten years ago: "The depressions in the freezing point obtained with naphthalene as a solvent at the elevated temperature of 79-80° C., suggest the probability that at this temperature triphenylmethyl exists partially in the dissociated, mono-molecular state, as the molecular weights obtained in this solvent are 407-420 against 486 calculated. On the assumption that such dissociation may exist, be it to ever so small an extent, the behavior of the hydrocarbon becomes intelligible: through the action of oxygen or of iodine the mono-molecular form reacts first, the equilibrium is thus disturbed and it can only be restored through further and further dissociation of the dimolecular triphenylmethyl until all of the compound has reacted."<sup>1</sup>

The dimolecular state of the hydrocarbon was, however, the occasion for the suggestion of various structures for triphenylmethyl all intending to do away with the interpretation involving the existence of a free radical. Markownikoff, Heintschel, Vorländer, Chichibabin, P. Jacobson, Baeyer, Flürschheim and others took part in the discussion, each suggesting a somewhat different structural formula for triphenylmethyl.

Thus, then, stood the question of the constitution of triphenylmethyl at the end of 1905: (1) The idea of the associated molecule, associated but none the less in equilibrium with the monomolecular free radical:  $(\text{R}_3\text{C})_2 \rightleftharpoons \text{R}_3\text{C} \cdot$ ; (2) the hexaphenylethane view, which assumed that hexaphenylethane, unlike all

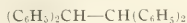
other saturated hydrocarbons, is, or rather ought to be, pre-eminently unstable; (3) Jacobson's quinol formula:



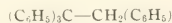
followers, but undoubtedly the free radical idea was most favored, and was most widely adopted.

*Constitution, Second Period, 1905-10*—We now enter upon the second period of our hypothesis. These questions presented themselves: Is it possible by *experimental* evidence to show whether a hydrocarbon of the type of hexaphenylethane *is* or *is not* stable? Is it possible to test experimentally the validity of Jacobson's suggestion?

One of the fundamental arguments in favor of the probable instability of hexaphenylethane was the well known fact that the unsymmetrical tetraphenylethane seemed impossible of preparation. Anschütz proved definitely that all methods, perfectly logical and reasonable in themselves, that have been employed by the many investigators in order to obtain the unsymmetrical tetraphenylethane, invariably resulted in giving the symmetrical compound:

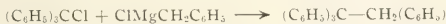


Symmetrical tetraphenylethane



Unsymmetrical tetraphenylethane

The conclusion became prevalent that the unsymmetrical hydrocarbon could not exist, owing to its instability. From the presumed instability of the unsymmetrical tetraphenylethane it was further surmised that the more complex homologous hydrocarbons, pentaphenyl- and hexaphenylethane, may reasonably be expected to be still more unstable and consequently less likely to exist as such. And yet, by the application of the more modern method, the use of the Grignard reaction, we were able to obtain any amount of the long sought-for hydrocarbon, *i. e.*, the unsymmetrical tetraphenylethane:



It turned out to be a very stable substance, beautifully crystalline, and showed no resemblance to triphenylmethyl.

The next step was to prepare pentaphenylethane, and here a number of difficulties were encountered. Finally, however, this hydrocarbon was also prepared by the action of magnesium simultaneously upon a mixture of triphenylchloromethane and diphenylbromomethane:



We encountered no difficulties in recrystallizing pentaphenylethane from the various solvents; no oxidation on exposure to air was observed, and neither iodine nor bromine added on. The successful preparation of the two higher phenylethanes above mentioned made it seem more probable than ever that the hypothetical hexaphenylethane ought also to be a *stable* compound and that it could be prepared if only the conditions requisite for the process could be found. Alas, neither we nor anyone else of the many who have tried it, have found these conditions. Hexaphenylethane still remains a figment of the imagination. And so the idea began to take root more and more generally that, after all, there is no difference between the so-called triphenylmethyl and the hexaphenylethane, that the former is in reality the latter. Add to this the insistent emphasis which Chichibabin laid upon his discovery (1907) that pentaphenylethane is decomposed by hydrochloric acid at 170° C., and that it absorbs oxygen at its melting point, 180°, and you have at least a *formal* analogy, if not a real one, between pentaphenylethane and triphenylmethyl. These two factors taken together, the failure to prepare a *stable* hexaphenylethane and the apparent lesser stability of pentaphenylethane than was attributed to it, these two factors had much to do with shaking the confidence of chemists that hexaphenylethane as such ought to be a stable

<sup>1</sup> Ber., 37 (1904) 2049.





of the actual, free triphenylmethyl radical, whatever its immediate predecessor. Soon after that many other analogues of triphenylmethyl were found to be monomolecular. The existence of free radicals, with C as trivalent, becomes therefore indisputable.

*Analogues of Triphenylmethyl*—As has been mentioned in the introduction, triphenylmethyl is but an example, the simplest example, of a large class of triarylmethyls. The three aromatic groups around the central carbon atom may vary to any extent: some may be nitrophenyl groups, or hydroxy-, methoxy-, brom-, carboxyphenyl, or they may be naphthyl groups. Also, as has recently been shown in our laboratory, one of the three aromatic groups may be replaced by the non-aromatic thienyl group,  $C_6H_5S$ . Furthermore, free radicals with a trivalent carbon atom have been obtained from compounds which belong to the following well known series:

Xanthone series (Gomberg and Cone); thioxanthone series (Gomberg and Cone); anthraquinone series (Liebemann); indene series (Kohler); thioindigo series (Kalb); acridine series (Cone); benzophenonesulphone series (Gomberg); etc.

*Historical*—Gay Lussac, in 1815, prepared for the first time cyanogen, and called it a "compound element," or a radical, because it behaved like an element in its reactions. He assumed the existence of the free cyanogen,  $CN$ , as a free radical. Wöhler and Liebig, in their classic paper in 1832, on the benzoyl radical, defined radicals very much as we do now, a group which remains

unchanged in a complex molecule through a series of chemical reactions. He did not claim the possible existence of "free" radicals, nor did he oppose such a view. Bunsen, in 1839-40, prepared the various derivatives of cacodyl: the chloride, oxide, etc., and the cacodyl itself, which he considered as a free radical,  $AsC_2H_5$ . Then followed the important work of Frankland, and of Kolbe, 1849-50. The former claimed to have isolated the radicals, *methyl*, *ethyl*, etc., by the action of zinc on the corresponding alkyl iodides, while Kolbe obtained the same radicals by the electrolysis of the sodium salts of acetic, propionic, etc., acids. In vain did Gerhard and Laurent insist that the molecular formulae of all these so-called radicals must be doubled, in accordance with Avogadro's hypothesis. The existence of free radicals was generally accepted as late as 1865, fifty years after Gay Lussac's introduction of this idea into chemistry. But in 1865, Schorlemmer showed by experimental evidence that Frankland's and Kolbe's methyl and ethyl were nothing else than ethane and butane. From that time on the question relative to the existence of free radicals was never seriously raised until the discovery of triphenylmethyl. What the future holds in regard to this new revival of the much disputed question is difficult to foretell. As a working hypothesis it has fully justified its existence—it has opened a new branch of organic chemistry.

UNIVERSITY OF MICHIGAN  
ANN ARBOR

## MORRIS LOEB MEMORIAL

The Morris Loeb Memorial meeting of the Chemists' Club was held in conjunction with the regular meeting of the New York Section of the American Chemical Society at The Chemists' Club, on Friday, March 6th.

A bronze bust of Dr. Loeb, executed by Mr. Karl Bitter, was presented by friends to The Chemists' Club. The presentation address was given by Dr. L. H. Baekeland, and the bust was accepted for the Club by President Charles F. McKenna.

A Morris Loeb Memorial volume prepared by a committee of the trustees of the Club was distributed to the members. This volume is a handsomely prepared book containing:

A REPRODUCTION OF A RECENT PHOTOGRAPH OF DR. LOEB  
RESOLUTIONS OF THE TRUSTEES OF THE CHEMISTS' CLUB  
RESOLUTIONS OF THE DIRECTORS OF THE CHEMISTS' BUILDING COMPANY

MORRIS LOEB AS A MAN, by L. H. Baekeland  
SCIENTIFIC CAREER OF MORRIS LOEB, by Charles Baskerville  
MORRIS LOEB AS A PHILANTHROPIST, by Maximilian Toch  
MORRIS LOEB AS A TEACHER, by Arthur E. Hill  
MORRIS LOEB AND HARVARD, Letter from Clifford Richardson  
MEMORIES OF A CLASSMATE AT HARVARD, Letter from J. D. Pennock

AN APPRECIATION, by Ellwood Hendrick  
BERLIN REMINISCENCES, by Walker Bowman  
A PERSONAL REMINISCENCE, by William J. Hammer  
TRIBUTE AT THE GRAVE, by Theodore W. Richards

### RESOLUTIONS FROM SOCIETIES

New York, Chicago and Washington Sections of the American Chemical Society  
New York and Canadian Sections of the Society of Chemical Industry  
New York Section of the Verein Deutscher Chemiker

### EXPRESSIONS OF FOREIGN SCIENTIFIC SOCIETIES

Imperial Academy of St. Petersburg      Universidade Do Porto  
The Faraday Society      R. Università di Bologna  
Sociedade Chimica Portuguesa

—[EDITOR]

### PRESENTATION ADDRESS

By L. H. BAEKELAND

MR. CHAIRMAN, LADIES AND GENTLEMEN:

One of the founders and most devoted members of this Section of the American Chemical Society was Dr. Morris Loeb.

He was also its first secretary, and in 1909, he was its chairman: a more efficient secretary or chairman never existed.

It seems timely to quote here some words from his opening address when he presided at these meetings.<sup>1</sup>

"Eighteen years ago, when the men who had carried the American Chemical Society through so many vicissitudes organized this section, in order that the general society might become a truly national one, I had the honor, rather than the duty, of being the first local secretary. The meetings were so poorly attended, the original papers so scarce, and the general business so unimportant, that no heavy work devolved upon its officers. We met in the chapel of the old university building, where Professor Hall and I had our primitive laboratories, out of which we carved, with some difficulty, shelf-room for the fragmentary society library. When we felt in need of a little variety, we sat in Professor Chandler's lecture-room in 49th Street and listened to the passing trains; or in East 23rd Street peered at the chairman ensconced behind batteries of Professor Doremus's bell-jars and air-pumps. An attendance of forty members, I believe, was a record-breaking event...."

The following paragraphs relate more particularly to his plan of founding the chemical museum:

"Every year scores of New Yorkers graduate in chemistry from our local institutions and return from years of protracted study in other American and European institutions. They are enthusiastic for research; in completing their theses they have laid aside definite ideas for subsequent experimentation; but they have no laboratory. While waiting to hear from the teachers' agency, where they have registered, while carrying on desultory correspondence with manufacturers who may give them a chance, they do not venture upon expenditure of time and money to fit out a private laboratory, which they may be called upon to quit any minute upon the appearance of that desired appointment. Often necessity or tedium will cause them to accept temporary work of an entirely different character and indefinitely postpone the execution of the experiments

<sup>1</sup> "Scientific Work of Morris Loeb," by Theodore W. Richards, Harvard University Press, Cambridge, Mass., p. 94.

which they had mapped out. Who will estimate the loss of scientific momentum, the economic and intellectual waste, which this lack of laboratory facilities for the graduate inflicts upon New York, as compared with Berlin, Vienna, Paris and London? Either our universities and colleges, or private enterprise, should provide temporary desk-room for the independent research chemist. . . ."

"There is still another point, however, in which the American chemist is at a great disadvantage as compared with the European: the ease of securing material for his research and of comparing his results with those of others. In Europe, especially in Germany, research is never seriously delayed by lack of a needed preparation, whereas none of our supply houses carry a full stock of chemicals.

To obtain a single gram of some particular substance, needed for a few preliminary tests, frequently causes weeks of delay, as well as the disproportionate custom house and brokerage expenses involved in the importation of small quantities.

Besides, owing to the better centralization of scientific laboratories in Europe, and the existence in each case of a fairly complete set of specimens accumulated in the researches of large numbers of academic investigators, it is comparatively easy to obtain by correspondence research material or typical specimens for comparison. In this country, on the other hand, laboratories are scattered throughout the numerous colleges and universities, and there are no established rules by which specimens must be deposited with the laboratory. In smaller laboratories, especially, the chances of preservation after the departure of the investigator are not very good. It would be, consequently, very much more difficult to obtain such specimens here. I would suggest, therefore,

that a chemical museum be established in New York, to perform for the American chemists the functions that the Smithsonian Institution so admirably carries on for the benefit of American naturalists. This museum would not attempt to be a popular show-place, but would embody, in the first place, as complete a collection as possible of chemically pure materials of the rarer kinds, so as to supplement, but not in any manner compete with, the stock of commercial supply-houses. Any scientific investigator would be entitled to borrow or purchase material required for immediate experimentation, and all used articles would be replaced as quickly as possible.

"In the second place, it would be a depository for specimens of new substances obtained in American research. Every

chemist would be invited to send to the museum a small quantity of each substance newly prepared by him, not, indeed, as an evidence of the good faith of his investigation, but, rather, to enable future workers to obtain such material, either for comparison, or for further experimentation with the least possible delay. Many substances that are now carried away from universities by students who subsequently abandon chemical research, or which belong to the families of deceased chemists who do not know what to do with them, would thereby be rescued from oblivion, and might ultimately become of the greatest value for a special purpose.

"Thirdly, this museum would invite chemical manufacturers to send standard samples of their products, and thereby facilitate the commercial relations between consumer and manufacturer.

"To such a museum there could be attached a competent staff of workers for the preparation of samples not otherwise available. In the analysis of samples submitted as official standards, we should have the beginning of that

*Chemische Reichsanstalt* which is now the chief object to which German chemists are directing their attention."

Later on, when through his enthusiasm, untiring energy and financial aid, the Chemists' Building had become an accomplished fact, he wrote as follows:<sup>1</sup>

"We have detailed some of the more striking advantages which the new building is expected to confer upon the chemical profession as a whole, as well as upon its individual votaries; is it an exaggeration to characterize the constitution of the Chemists' Building Company itself as a new era in the chemical industry of our country? In scanning the list of shareholders, we find representatives of nearly every important concern,

or even the larger companies themselves; but that this is not a 'trust,' in the sense so obnoxious to the yellow journalist, is demonstrated by the conditions of the partnership. No shareholder can receive more than 3 per cent dividends, and the surplus cannot, under any circumstances, accrue to his benefit within the next fifty years. This association, therefore, is not for individual profit, but for the raising of the standards of chemical industry and research in the United States. If we recognize what the Verein zur Hebung der chemischen Industrie, founded by Hofmann and Werner Siemens, has done for Germany, we may well hope for further fruits of this initiative here. Perhaps this building will house joint laboratories

<sup>1</sup> Theodore W. Richards, *loc. cit.*, p. 126, etc.



MORRIS LOEB BUST

for the solution of questions affecting all manufactures alike; or experimental stations for the study of natural products not yet utilized; or a cooperative bureau of standardization for analytical methods; or a national welfare bureau for employees in chemical factories. This building does not owe its erection to some benevolent demigod, extending his protecting wing over people unable to care for themselves; it is a building by the chemists, of the chemists, and for the chemists. May it ever serve as an exemplar of unselfish patriotic cooperation!.....

"For, strange as it may seem to the layman, who has seen the ugliest blots on a landscape designated as chemical factories, who has sniffed with disgust a chemical odor, has been urged to believe that the chemist's shadow contaminates pure foods, and has been taught in school that alchemy spelled fraud and sorcery, *our science is one calculated to develop the ideal side of human nature, and the chemist, more perhaps than the votary of natural science or the devotee of the so-called humanities, is led to an intense interest in human development.*.....

"Our science aspires not only to know, but also to do. On the one hand, it leads us to delve into the secrets of nature, in the minute atom as well as in the far distant stars, in the living cell as well as in the crystallized relics of the convulsions from which this earth was born; on the other, it leads us to apply this knowledge to the immediate needs of man, be it in safeguarding his health, in ministering to his material or esthetic wants, or in regulating his commerce and in facilitating his utilization of the earth's resources..... There are two ways of aiding a man or a cause: by addition to the income or reduction of the expense. The pecuniary result to the beneficiary may be the same, but the moral one is far different; it is not only the beggar who is pauperized by the cash gift and uplifted by the aid which enables him to earn his own livelihood. Arts and sciences may be stimulated by prizes and scholarships beyond a doubt, but the relation between donor and recipient is not free from restraint, and the probability of human error in the selection of the right incumbent makes the method a wasteful one at best.... To remove these disadvantages in time and cost, to provide easy access to books and apparatus, to make room for the independent scientific worker, are the ideals which hovered before the eyes of those who planned this present enterprise. Time will show whether they can all be realized, but whatever is done in this beautiful building, which we are about to dedicate, must open free opportunities to all and show favoritism toward none, if the trust imposed upon its management be administered in the spirit of those who have contributed toward its erection....."

After his untimely death, which left so many in sorrow, it was found that by his will, he had planned the realization of the ideals he had preached.

To his University, Harvard, he left a large sum of money for chemical research; to the Chemists' Building, he gave all his shares; to the American Chemical Society, he left a fund for the creation of a chemical museum along the lines conceived and clearly described by him.

Mr. Chairman, none of us, who have known Morris Loeb, who have lived, worked, or spoken with him, need a bust nor a portrait to remind us of the man, or his work. But as we grow older and death keeps thinning out our ranks, younger generations of chemists will use these halls. Our duties, our responsibilities, will become their duties, their responsibilities.

I have no doubt that their aims for good, will be of the highest; that they will better realize than the present generation, that to be a chemist, is to be an apostle of Progress and Civilization, of Justice and Truth. But the chemists of the coming generation will not have known Morris Loeb, and we must remind them of what one of our generation dreamt, planned and did for them. This is the reason why some friends of Dr. Loeb obtained a bronze bust from Mr. Karl Bitter, an artist whose

reputation is no longer to be made. It is their desire that this bust should adorn the halls of The Chemists' Club.

Dr. McKenna, upon you, as President of The Chemists' Club, devolves the responsibility of placing this bust where it will best serve its purpose.

#### ADDRESS OF ACCEPTANCE

By CHARLES F. MCKENNA

Dr. Baekeland and his generous friends have placed The Chemists' Club under a lasting debt of gratitude.

Ever since the death of Doctor Loeb the officers and members of the Club have repeatedly wondered how we should be able adequately to put on record here all that his name implies in our history.

Doctor Loeb left his impress upon many spheres of activity in the world that he was fated to leave early—on philanthropy, civics and education among the most noteworthy ones. But chemistry was his deepest love, and that science received most from the labor of his hands and the genius of his mind. Particularly did this agency which we find most forceful in the profession today, and which is known as The Chemists' Club, receive much from his generous impulses and constructive mentality. He gave to this club his best, not that it might be merely a social agency, but that it should be even more, a strong, suggestive, creative power in the purest realms in the science.

As you have heard from Dr. Baekeland's address, in all of the discussions which took place during the inception of this enterprise, Doctor Loeb was constantly insisting that provision should be made for furnishing facilities for research to scholarly chemists who had given proof of their devotion to the science and their possession of a field worthy of deep study.

I speak for the officers and members of the Club when I pledge its honor that in loving memory of Morris Loeb the same generous readiness with help shall always mark its attitude towards the scholar in chemistry.

The consequences of his activity will thus be read into the pages of American chemical history, and the glory of the discoveries to be made here shall reflect back to him.

It is pleasing, when depositing this bust in a place of honor in a chemists' hall, for us to know that it is a work of art, and that it is of bronze, the most enduring of monumental materials. Marble is fragile and cold; bronze is resistant but strangely attractive. To chisel in stone must be a hazard of skill; to model and mould and affectionately retouch the casting must be a satisfying art. Therefore all the world loves this metal. This beautiful specimen has been produced as a labor of affection, and Mr. Karl Bitter has put his best into it and given freely and gratuitously to The Chemists' Club the benefit of his artistic spirit.

It was my good fortune last week to listen to an address by Mr. Bitter upon the methods of sculpture in ancient times compared with those of modern times, and I have never been more charmed and instructed, and there is no one today so well fitted to give us this enlightenment. He is not only a master of his art, but he has that love that lingers over the triumphs of his history.

Therefore we appreciate the more the value of this bronze so thoughtfully secured for us by Dr. Baekeland and his friends.

The hand of a genius who is fit to stand beside the immortal sculptors of the ages has modeled it; its noble substance will preserve it, the *patine* of time will beautify it. What could be more pleasing to us all than thus to honor the memory of Morris Loeb, the idealist, the scholar, the lover of his fellow man?

Further to mark this sense of obligation that we feel, the Club has had a Committee at work preparing a literary memorial of our friend. It is beautiful in typography and in form, and contains the words of affectionate remembrance and regard which poured forth so sincerely when his friends in these circles wished to express their grief over his death. We take pleasure in making a distribution of this volume as far as we can make a limited edition go.



## OBITUARIES

## ROBERT KENNEDY DUNCAN

By the death of Dr. Robert Kennedy Duncan on February the eighteenth, American Industrial Chemistry lost one of its greatest members and, what will be harder to replace, the American chemist lost one of his greatest friends. Much of Dr. Duncan's activity had, as its avowed purpose, the betterment of the conditions under which the American chemist works. He also promoted American chemistry in another and broader way; his literary interpretations of scientific facts aroused a world-wide interest in the subject of chemistry—he gave life to the most abstruse ideas of cold science and made them peculiarly fascinating to the reader.

Robert Kennedy Duncan was born in Brantford, Ontario, November 1, 1868. He was of Scotch-Irish descent and in his character he showed many of the best characteristics of both races. His disposition was happy and he was a brilliant and witty speaker and writer; his Scotch ancestry was shown in an almost uncanny farsightedness. Dr. Duncan received the degree of B.A. from the University of Toronto in 1892 with first-class honors in Physics and Chemistry. He was fellow in Chemistry in Clark University 1892-3 and a graduate student in Columbia University 1897-8. He was instructor in Physics and Chemistry in the Auburn (N. Y.) Academic High School 1893-5, Dr. Julius Sachs' Collegiate Institute (N. Y.) 1895-8 and the Hill School, Potsdam, Pa., 1898-1901. He studied abroad in the years 1900, 1903, 1904 and 1907. His first college teaching was with Washington and Jefferson College, where he was Professor of Chemistry from 1901 to 1906.

In 1906 he attended the Sixth International Congress of Applied Chemistry in Rome and it was in this historical old city of Rome that he conceived the idea of a practical method of bringing the learning of the University to the service of Industry. He once told me that the whole system of Industrial Fellowships which has since become a living reality in the Mellon Institute flashed then into his mind—even to the minutest detail—as he stood overlooking the eternal hills of Rome. In 1906 he was called to the University of Kansas as Professor of Industrial Chemistry and it was there that he started in a small way his unique system of Industrial Fellowships. The work

began modestly with a few Fellowships of \$500 a year each. As industrialists began to see the results obtained and began to realize what a privilege this system offered to them, the Fellowships grew by leaps and bounds until a single one has \$15,000 per year and the Mellon Institute is now receiving \$103,000 per year from industrialists to be used towards the solution of difficult problems of vital and immediate interest to the donating corporations. I can best express in his own words the ideas which were in Dr. Duncan's mind when he proposed to make the University of direct service to Industry.<sup>1</sup>

"It (the learning of the University) could enter the factory only through the employment therein of men of high scientific and technical training, working in an atmosphere conducive to success—men who were genuine researchers inspired to solve practical problems. The universities of the country were not providing the industries with men of such qualities. It is true that they were sending out large numbers of men—chemical engineers, etc.—on the basis of a four years' college course, but such men were merely *taught* men; they were not researchers, and under the conditions of contemporary factory practice were deprived of the possibilities of development, and were, in fact, for the purposes of research merely ruined. The genuine researchers turned out by the universities, young doctors of philosophy with a record of successful academic research and with a proved capacity for creative work, were discouraged by the universities of any ambition to enter applied research and were led to consider the teaching profession as the only logical goal. A man of splendid training and of brilliant research qualifications who entered applied

science—among whom are the few contemporary first-class research technologists—did so under the onus of academic disapproval. The reason for this lay in the fact that American science had, through generations, been built upon the basis of severe academicism and formalism. It was deemed contrary to university ideals and traditions that research should have in view any utilitarian end; there was great insistence upon *pure* science, the implications being that applied science was *impure* and constituted a degraded form of research."

I wish to dwell particularly on another phase of this system

<sup>1</sup> *Journal of the Franklin Institute*, January, 1913



ROBERT KENNEDY DUNCAN

of Industrial Fellowships as it throws light on the predominant trait of Dr. Duncan's character. This scheme gives to young men—the researchers—most unique opportunities. They have a chance to prove that they can do things and to prove it directly to the men who are the executive heads of business. When they have thus proved that they belong to the "can do" class, industry at once opens to them positions that they could in the ordinary course of events hope to obtain only after many years. Dr. Duncan often said to me that while he fully appreciated the value of this system of Industrial Research to the University and to Industry and to the Public, yet he felt his keenest pleasure of achievement when he thought of the opportunities which he was able to offer to young men. This was significant of the spirit of the man. He was always thinking of others. He sought nothing for himself, but did not hesitate to perform any amount of labor which might possibly advance one of his "boys." While a matchless executive, he was to his associates and the Fellows of the Institute more like a father or an older brother than a director. It was this spirit of unselfish love which he tried to inculcate into his laboratories and he always felt that the phenomenal success of this work was largely due to the spirit which was maintained in the laboratories.

There will be no question in any one's mind as to the place Dr. Duncan occupied as an interpreter of new scientific knowledge. His books, "The New Knowledge," "The Chemistry of Commerce," and "Some Chemical Problems of Today," as well as many shorter articles in the magazines—notably Harper's—represent a class of literature of the highest scientific accuracy and are written with a sweeping charm that maintains the reader's unbroken interest from start to finish. As an interpreter of the new knowledge in his chosen field of activity he ranks—and the world will accord this to him—coordinate with Tyndall.

His attitude towards matters of religion reflected the best thought of our time. Thoroughly trained in the natural sciences and possessed of a most brilliant mind capable of the most accurate cold reasoning, he retained throughout his life a child-like faith in the fundamentals of Christianity. Calmly and courageously he met death. It was to him—and he gave utterance to this two days before his final departure—but "a step over a little rill from one life into a greater life."

Dr. Duncan was called to the University of Pittsburgh as Director of the Department of Industrial Research in 1910. In March, 1913, this Department became, through a magnificent gift from Messrs. Andrew W. and Richard B. Mellon, the Mellon Institute of Industrial Research and School of Specific Industries of the University of Pittsburgh. Dr. Duncan felt that he was fortunate in that he was permitted to live to see his life work an established fact. He realized during the last two years that he might not live long and with his usual farsightedness he carefully trained those who were to take up the work after he was gone. It was his wish that the greater Mellon Institute should be his monument and those of us on whom the responsibility falls are trying to follow the same line of enthusiastic and conscientious endeavor which he originated, that there may thus be erected a living memorial to a man who so richly deserved it.

RAYMOND F. BACON

#### GEORGE WESTINGHOUSE

"George Westinghouse is in character and achievement one of the great men of our time."—LORD KELVIN.

A man who was rivalled only by Andrew Carnegie in his contribution to the industries of this country and one who walked among the mighty in the history of the electrical art died in New York on March 12th. George Westinghouse had been a leading and honored figure in Pittsburgh for the space of an

average lifetime; and for the greater part of that time he had enjoyed world-wide reputation as one of the leading inventors of the age.

Mr. Westinghouse was born in Central Bridge, N. Y., on October 6, 1846. His father was an inventor, and from him undoubtedly were inherited the qualities which made the younger Westinghouse great. After an honorable service during the Civil War, he returned home and engaged in industrial work. As a mere boy he had devised a rotary engine with improved features; but what was probably his first original invention was a machine for hoisting derailed cars back on the tracks. The idea of the airbrake was suggested to him by delay in a journey due to a collision. He worked on this plan for several years; and in 1868 made arrangements for the manufacture of the first airbrakes, which were successfully tested in the latter part of that year. This was the first of the great Westinghouse patents. It developed with the growth of the railroad system and its adoption spread all over the world. The Westinghouse Airbrake Company is now one of the established institutions of Pittsburgh. Over forty years ago, Mr. Westinghouse introduced to this country the Saturday half-holiday: the 54-hour week for employees was started by his Airbrake Company in 1869 and has since been widely adopted.

In 1883, Mr. Westinghouse became interested in railway signals, and invented the system manufactured by the Union Switch and Signal Company. This was an invention second in importance only to the airbrake. In 1883 he devoted his attention to electrical distribution, and, by the purchase of some patents and the devices of others, began the business which, in 1891, was consolidated into the Westinghouse Electric and Manufacturing Company. This development included the manufacture of electrical machinery, for which the Westinghouse Machine Company was organized under the presidency of his brother. The Westinghouse Company constructed the first generators for transmitting the water-power from Niagara Falls. About 1888, Mr. Westinghouse, recognizing the industrial importance of natural gas, commenced drilling operations in Pittsburgh, and struck a well that produced a high pressure of gas. This took him into the gas business, which was organized under the Philadelphia Company. In 1892 the importance of incandescent lamps led to the organization of the Westinghouse Glass Factory.

The last five years were a period of revirescence—the most active and productive of George Westinghouse's life. During that time he developed the geared turbine and the air spring inventions, and he also succeeded in securing the adoption of his plan for the reorganization of the Electric Company which bears his name.

These are but leading features in a great inventive and industrial career. The entire group of Westinghouse industries consists of 35 companies, with a capitalization of \$150,000,000, with factories covering 200 acres of floor space and giving employment to an average of 16,000 persons. In these interests are owned over 3,000 patents. The world-wide benefits of his genius compelled the establishment of great industrial branches in England, France, Germany and Russia, the airbrake invention in particular demanding these extensions.

Owing to his many achievements in mechanics, electrical engineering and applied industry, the name of Westinghouse was known the world over, and consequently George Westinghouse had many honorable distinctions conferred upon him. His alma mater, Union College, conferred upon him the honorary degree of Doctor of Philosophy. He was decorated with the order of the Legion of Honor, with the order of the Royal Crown of Italy, with the order of Leopold of Belgium. He was the second recipient of the John Fritz medal. He received the degree of Doctor of Engineering from the Königliche Technische Hochschule of Berlin. He was an honorary member of the

American Society of Mechanical Engineers, of which body he was also president in 1910. He was one of the two honorary members of the American Association for the Advancement of Science, and was also an honorary member of the National Electric Light Association of America. He was awarded the Scott premium and medal by the Franklin Institute; he received the Edison gold medal for meritorious achievements in the alternating current system of electrical distribution, and was also the recipient of the Grashof gold medal from the Society of German Engineers.

While Mr. Westinghouse's industrial affairs were vast, his

personal traits were admirable. He was cultured and was charming in his personal relations. Physically cast in a large mold, his mind and heart were equally large; he was an unostentatious, kindly, helpful and hard-working man, whose sturdy characteristics were admired in all countries. Naturally a man of immense dynamic force, his energy was supplemented by a boundless tenacity of purpose, a splendid optimism, and an abiding faith in himself. There have been few men who accomplished so much and ended life with such a record of distinguished services in the advancement of industry.

W. A. HAMOR

## CURRENT INDUSTRIAL NEWS

By M. L. HAMLIN

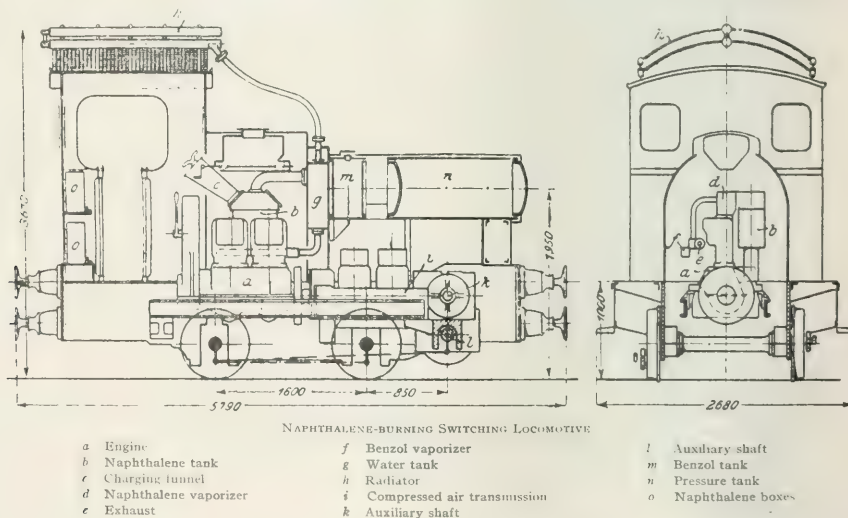
### NAPHTHALENE AS A FUEL FOR MOTOR VEHICLES

In the *Zeitschrift des Vereines deutscher Ingenieure*, 58 (1914), 22, appears an article by A. Heller in which he discusses the question of fuel for motor vehicles in general, and describes two attempts made in France to use naphthalene—one in a taxicab and the other in an internal combustion yard locomotive.

The great increase in the use of internal combustion engines for automobiles of all kinds has of late brought up the question of fuels, which is all the more pressing because the supply of gasoline has not been able to keep up with the increasing demand. The increase in price of gasoline is a result of this and is not due to price manipulation. The comparative decrease in the output of gasoline is due to two conditions: (1) America has hitherto furnished about 80% of the world's supply, but lately, partly

price has in the meantime risen, so that it can no longer compete with gasoline as it once could, and in any case the available German output is small. Its present assured price of 7.5 cents per kg. is far above that which would permit of its development for industrial uses.

Under these circumstances it is strange that more attention has not been given to naphthalene, since its practicability as a fuel has long since been proved by the Gasmotorenfabrik Deutz, and it is produced in very large amounts. Pure naphthalene ( $C_{10}H_8$ ) has a specific gravity at 15° C. of 1.15, and melts at 79.7°, while crude naphthalene melts at about 75°. Its heating value is 9700 calories per kg., only slightly different from that of gasoline, but its higher percentage of carbon (93.7% C.; gasoline, 92.3% C.) requires more air for combustion.



because of the enormous increase in the number of automobiles in America, her contribution has fallen off; (2) in the rest of the world, as well as in the United States, the gasoline supply has not kept pace with the demand, because in spite of the increased output of crude oil, a continuously heavier product seems to be obtained, and attempts to improve the yield of gasoline artificially, e. g., by cracking, or to obtain suitable fuels from natural gas by treatment under pressure, have failed to better the situation.

The search for a suitable fuel led, after the use of alcohol had been proved uneconomical, to benzene; while it has been proven a success mechanically by the Daimler Motor Company, its

The chief advantage of naphthalene is its cheapness; with an increased demand for it, a price of 2.5 cents per kg., one-third that of benzene, can be counted on. The mechanical difficulties of its use are not so great that they cannot be overcome, although the radius of action of vehicles using naphthalene must be somewhat limited because it has to be carried in the bulky form of a solid.

The only reported experiments with naphthalene as a fuel for motor vehicles come from France. In one case [*Le Poids Lourd*, 9 May, 1913] a taxicab engine and in the other [*Le Génie Civil*, 31 May, 1913, *Mém. Soc. Ing. Civ. de France*, April, 1912] a yard locomotive was modified to burn it. The taxicab (a



Renault machine) had a two-cylinder, 12 H. P. engine of 10.2 cm. bore and 12.0 cm. stroke. A preheater, heated by the exhaust, and a special vaporizer were built in. Under the supervision of officers of the Conservatoire des Arts et Métiers in Paris, a round trip of 105.4 km. was run. The average speed was 34.4 km. per hour, and the maximum 42.3 km. per hour, 14,996 kg. of naphthalene were used, or 0.142-kg. per km., which, at a price of 2.5 cents per kg. would mean 0.335 cent per km., as against 1 cent per km. for gasoline. The engine was run 13 min. 37 sec. on gasoline before the naphthalene was turned on, and could be started without gasoline after a 10 min. stop or by priming the cylinders with gasoline after a 16 min. stop. Further than this there were no difficulties; the exhaust was almost smokeless and there was no deposit in the cylinders.

The second experiment was with a yard locomotive (shown in the figure) built by Schneider & Co. of 19 metric tons service weight and 2500 kg. maximum tractive power. It had four cylinders, cast in pairs, of 14 cm. diameter and 20 cm. stroke. With benzene it developed 72 H. P. at 100 r. p. m. and used 280 g. per H. P. per hour. The cooling water was circulated by convection and passed through a jacket around the naphthalene container *b*, keeping the fuel molten. The liquid naphthalene was pumped from the container to the vaporizer above the cylinder head. Raw naphthalene at 2-2.5 cents per kg. was used.

The results of the tests were favorable and showed the machine practical, but more exact data are not yet at hand.

#### REMOVAL OF BLAST FURNACE OBSTRUCTIONS WITH EXPLOSIVES

According to H. Schöneweg, *Zeitschr. ges. Schiess- u. Sprengstoff*, 8 (1913), 445-448, obstructions which completely prevent the passage of the blast in blast furnaces may be removed by dynamite without injuring the furnace. The charge is usually about 600 g. but may be as large as 1,250 g., provided it is exploded 40-50 cm. from the furnace wall. The dynamite is fired by a fuse, the charge being contained in a tube enclosed in a second tube (in which it must have free play) projecting through a hole drilled in the furnace wall.

#### TRANSPORTATION OF CHEMICALS BY WATER

In *Chem.-Ztg.*, 38 (1914), 146, J. Aeby discusses the above problem from the point of view of the transportation expert in the light of the lessons learned from the Voltorno disaster. In the English investigation of this accident it appeared that barium peroxide was the original cause of the fire; therefore, there is, the author believes, danger that this product will be boycotted and its transportation by water surrounded with difficulties, as is already the case with sodium and potassium peroxide. Admitting that barium peroxide was the primary cause, he however points out that the fire would never have occurred unless this substance had been shipped with inflammable organic substances. Since it cannot be expected that transportation companies and steamship lines shall have expert chemical knowledge of the goods they carry, the author considers it the duty of shippers, in their own and the public's interest, to advise the transportation companies as to the nature of goods shipped, so that for example, neither peroxides nor permanganates shall be shipped in the same cargoes as inflammable organic substances, strontium nitrate, etc.

#### A NEW GERMAN SILK MILL

Michels & Cie have recently built a new silk mill at Nowawes, near Berlin, which is described in the *Zeitschrift des Vereines deutscher Ingenieure*, 58 (1914), 6, 53. Aside from the mechanical perfection of the plant, its appearance has not been neglected,

great pains having been taken to make the building and its approaches artistic. These efforts towards beauty are considered to have a direct advertising value and so are economically justified. They are helped by the fact that the shed type of factory with its ugly saw-tooth roof was abandoned in favor of one with a large central skylight, which assures each machine a supply of diffused daylight without shadow. All the machines are driven by individual electric units, which receive current from the power plant in the lower story. The piping and wiring pass for the most part through this story, so that necessary repairs will cause the least possible interruption of manufacture. The ventilating, heating and humidifying systems are so designed that the air can be changed in winter once, in summer four times per hour. The whole plant cost \$170,000, of which \$40,000 was spent in preparing and improving the grounds.

#### WHALE OIL

H. T. Offerdahl-Larvik gives the following facts about whale oil in *Ber. d. deutsch. Pharm. Ges.*, 23 (1913), 558-559: The world's output in 1912 was 1,200,000 bbl. of (750 kg. each), more than half of which came from the Norwegian fisheries. In 1904-1905 the cost of producing 1 ton of oil was \$67.50; in 1912, owing to higher wages, \$94.50.

After the first separation of the oil, the flesh and bones are dried at 300°-400° C., re-pressed, and used for fertilizer. This contains 10-12 per cent nitrogen, 14-15 per cent phosphoric acid, and not more than 3 per cent oil if it is of good quality. Whale oil is now hydrogenated exclusively for soapmaking, but the author believes it has a value as a foodstuff, and that the nickel present, left after the hydrogenation, is absolutely non-toxic.

#### ITALIAN AUXILIARY MARINE DIESEL ENGINE

In *THIS JOURNAL*, 6, 259, an account was given of a passenger vessel equipped with large Diesel engines. At the time of the adaptation of this type of engine to marine service it was freely predicted that a new era of prosperity was in store for the auxiliary sailing vessel, and this prediction has to some extent been fulfilled. One of the latest vessels of this type is the Italian three-masted schooner "Aosta," 1050 tons, described in *Engineering* (London), 97 (1914), 182. Her engine is of the two-stroke-cycle type with four cylinders of 350 mm. (13.75 in.) diameter and 500 mm. (19.7 in.) stroke, giving at 200 r. p. m. about 440 brake horse power, corresponding to the comparatively high mean effective pressure of 127 lb. per sq. in., assuming the engines to have a mechanical efficiency of about 73 per cent. The engine is a good example of modern Italian engineering practice and is unique in almost all its principal features.

#### LOCAL SURFACE HARDENING OF HIGH TENSION STEELS

According to *Engineering* (London), 97 (1914), 212, Messrs. Vickers have perfected at their River Don Works, at Sheffield, a system of surface-hardening which can be applied to any local part of any casting or forging of high-tensile steel, without involving distortion and without destroying the effects of the usual heat treatment to which the whole casting or forging may have been subjected. The equipment includes merely the outfit usually supplied for oxy-acetylene welding purposes; four sizes of burners meet all general requirements. The work to be hardened locally is placed in a tank of water with adjustable overflow, so that the water-level can be regulated, as while the portion of the surface being hardened is instantly heated to the required temperature, the whole of the remainder of the article is kept as cool as possible by being immersed in water. Should this be impossible, the part not being hardened must be kept cool by water flowing over the surface. The burner is held so

that the outer portions of the flame flow in the direction along which the burner is traveling, and the portion of steel heated should be cooled—when intense hardness is required—by arranging that cooling water shall follow as closely as possible the traveling burner, but not so close as to disturb the flame, because that is not only liable to put it out, but prevents rapid heating and causes irregular hardening. The cost for hardening each square inch of surface is approximately only 0.5 cent.

The flame required must be of the highest possible temperature, and burn close to, and even under, water. This is obtained by adjusting the flame as for welding, and then increasing the pressure of oxygen, so that the flame changes color and appearance from a white cone to a bluish streaked tongue, when observed through smoked glasses.

The essential to success in this method is the speed of heating. As the flame passes along, the surface is instantly cooled by the cold remainder of the forging or casting, leaving it of the maximum hardness of which the steel is capable when heated and quenched in cold water. To obtain a thin but intensely hard surface, the part to be hardened should be just below the surface of the water, the impinging flame blowing the film of water away. The normal depth of hardening is about  $1/16$  in., but a greater depth, up to about  $1/8$  in. or  $3/16$  in., can be obtained by slightly prolonging the heating, a slight wavy or rotary movement being given to the flame to avoid burning the surface of the steel.

Contrary to what might have been expected, even with the hardest steels, there is no tendency for the hardened surface to crack or flake away from the unhardened portion. In a number of cases made for examination, not a single instance shows any parting between the hardened and unhardened portions.

While Messrs. Vickers are applying the process only to high-tensile steels, and are interested in no further application, it is of general engineering interest to note that cast-iron and "Black-heart" malleable-iron castings can also be given a glass hard surface by hardening in this manner.

## THE SPONTANEOUS COMBUSTION OF COAL IN MINES

The question of spontaneous combustion of coal in mines is discussed in *Engineering* (London), 97 (1914), 224, and the results of an English government investigation are reported. In August, 1912, the Home Secretary appointed a Departmental Committee, consisting of Mr. R. A. S. Redmayne, Chief Inspector of Mines, Sir Arthur B. Markham, M. P., and Messrs. C. E. Rhodes, Frank Rigby, and Herbert Smith, for the purpose of inquiring into the circumstances in which spontaneous combustion of coal occurs in mines, its causes, and the means of preventing it or dealing with it.

Considering that colliery temperatures vary widely from colliery to colliery, the committee, after taking much evidence from the inspectors, managers and men, suggest that the Inspector of Mines should be notified: (1) when gob stink or other signs of combustion are observed; (2) when the air temperature in any accessible part of the mine is  $20^{\circ}$  F. above the normal temperature in the main return air-way, or when it rises to  $110^{\circ}$  F.; (3) when any flash has been observed coming from any pack or waste. Notification should also be made of the commencement of work for the purpose of discovering or combating a fire or anticipated fire.

The members of the committee, recognizing the importance of special conditions, propose that in all the mines, in which safety lamps are used, or in which as much as  $1/4$  per cent of inflammable gas has been found in any ventilating district or return air-way of the mine, on any one occasion: (a) When smoke or other signs of a fire occur, all the workmen should at once be withdrawn from the affected ventilating district, and not be re-admitted before the manager and two representatives of the men have made an inspection and have

entered their opinion, duly signed, that the mine is safe again; (b) when the actual fire has been located, or is known to exist, all the men working on the seam, and on other seams worked on the same level, should be withdrawn from the mine, except those engaged in fighting the fire, unless the seam be naturally wet throughout, etc.; (c) in the event of a fire being dammed off, all men should be withdrawn until the work has been completed.

As regards rule (b), four members would be ready to relax this rule provided incombustible dust be used on the roads; but they would require, in parts contiguous to the fire, at least four parts of stone-dust to one part of coal-dust; that is to say, they would insist on more stone-dust than the Explosion in Mines Committee deems necessary. Four members again recommend in memorandum 5 that all timber should be removed from wastes and roads to be abandoned, as that timber is clearly a very fruitful source of danger.

Finally, Mr. Herbert Smith, who had signed only the first two memoranda, deprecates the use of stone-dust, which must be injurious to the health of the miners. In South Africa, he points out, the working life of a miner is four or five years, and the mortality in the Yorkshire ganister-mines is also very high and medically ascribed to dust inhalation.

## SOME STATISTICS ON GERMAN UNIVERSITIES

Some interesting statistics about German universities are given in the *Chemiker-Zeitung*, 38 (1914), 250. During the academic year, August, 1911–August, 1912, 4455 doctors' degrees were given, 83 more than in the previous year; these were divided among the various faculties as follows: Theology, 55; law and political science, 1265; medicine, 1343; philosophy and natural science, 1792. The percentage of students who receive degrees in the different universities and faculties varies from 87.6 per cent in law at Erlangen to 0.2 per cent in law at Berlin.

The salary of rector varies in an astonishing way at different universities. This position is of course quite different from that of president in an American university, for the rector is elected from the faculty by his colleagues for a short term. In Berlin the rector's salary is about \$9,250, in Kiel \$800, while in the Academy at Braunschweig it is slightly more than \$20. The average is about \$1,500. The salary of the deans of the various faculties varies even more, ranging from \$5,500, the salary of the dean of the faculty of philosophy at Berlin, to \$5, the compensation of the head of the theological faculty at Halle.

## DÜSSELDORF CENTENNIAL EXPOSITION

The centenary of the annexation of the Rheinland by Prussia will be celebrated in 1915 by an exposition at Düsseldorf. According to the *Chemiker-Zeitung*, 38 (1914), 223, chemical and pharmaceutical industries will be represented more fully than ever before. In the chemical section a special effort will be made to show the history and development of pure chemistry during the century, its connection with other sciences and particularly with various industries.

## THE RUBBER SITUATION IN JAPAN

The rubber industry in Japan is in a very depressed condition. It takes a leading place among those industries that have grown up under the protective tariff and there are now about thirty firms with a capital of \$2,300,000, engaged in it, but this very condition has reacted with the extremely limited demands of the market to cause a large drop in the price in the last two years. Although the price of raw material has also dropped, according to the *Chemiker-Zeitung*, 38 (1914), 134, the Japanese manufacturers have not yet felt the benefit of this; they are making no profits now and all except the strongest companies face the prospect of heavy losses in the future.

## ENGLAND'S CHEMICAL TRADE 1912 AND 1913

Chem. Ztg., 38 (1914), 240

Imports	VALUES IN ROUND THOUSANDS	
	1912	1913
Sodium compounds	\$ 802,000	\$ 860,000
Salt peter	1,086,000	1,205,000
Other potassium salts	3,096,000	3,151,000
Fertilizers: Basic	446,000	510,000
Bone	1,088,000	1,098,000
Guano	408,000	746,000
Chile salt peter	6,374,000	7,453,000
Phosphate and rock phosphate	4,708,000	4,371,000
Bleaching materials	219,000	172,000
Boracite, borates, borax, etc.	936,000	1,015,000
Sulfur, crude	562,000	464,000
Calcium carbide	950,000	1,362,000
Chemicals, e. g., Acetone, calcium acetate, sulfuric acid	7,770,000	8,595,000
China bark	245,000	290,000
Quinine and its salts	477,000	512,000
Other drugs	6,959,000	6,515,000
Acetic acid	419,000	429,000
Tartaric acid	1,118,000	1,237,000
Cream of tartar	1,626,000	1,660,000
Glycerine: Crude	1,315,000	1,274,000
Distilled	457,000	478,000
Coal-tar products, not dyes	789,000	822,000
Aniline and naphthalene	7,318,000	7,713,000
Other coal-tar dyestuffs	2,000	2,000
Color extracts	693,000	642,000
Other dyes	1,396,000	1,501,000
Alizarine and anthracene dyes	1,319,000	1,361,000
Indigo, natural	493,000	275,000
synthetic	454,000	383,000
Catechu	537,000	358,000
Tanning materials: Bark	1,120,000	1,740,000
Gambier	684,000	719,000
Myrobalanen	813,000	834,000
Sumach	502,000	416,000
Valonea	761,000	821,000
Other tanning materials	39,000	86,000
Barium sulfate	808,000	752,000
Nickel oxide	585,000	451,000
Red lead	344,000	316,000
White lead	1,762,000	1,815,000
Zinc oxide	2,075,000	2,147,000
Pigments, not specified	4,143,000	4,281,000
<b>Exports</b>		
Sulfuric acid	231,000	313,000
Salt (not table salt)	2,269,000	2,363,000
Sodium carbonate	2,793,000	2,818,000
Sodium bicarbonate	713,000	612,000
Sodium chromate and bichromate	259,000	297,000
Sodium sulfate	438,000	573,000
Caustic soda	3,786,000	3,618,000
Soda crystals	220,000	226,000
Other sodium compounds	764,000	789,000
Salt peter	261,000	233,000
Potassium chromate and bichromate	462,000	406,000
Other potassium compounds	469,000	655,000
Ammonium chloride	806,000	637,000
Fertilizers: Ammonium sulfate	19,956,000	22,060,000
Superphosphate	112,000	123,000
Basic slag (Thomas Meal)	1,172,000	1,320,000
Other fertilizers	4,166,000	4,648,000
Copper sulfate	8,597,000	8,514,000
Bleaching powder	849,000	953,000
Tartaric acid	366,000	450,000
Chemicals, misc.	14,083,000	13,160,000
Opium	332,000	62,000
Quinine and its salts	338,000	363,000
Other drugs	10,512,000	11,330,000
Glycerine, crude	1,614,000	2,213,000
distilled	1,654,000	1,893,000
Petroleum	153,000	123,000
Aniline and toluidine	162,000	145,000
Anthracene	39,000	7,000
Benzene and toluene	955,000	1,515,000
Carbolic acid	1,046,000	953,000
Tar, crude	91,000	89,000
refined	233,000	346,000
Naphthalene	113,000	188,000
Pitch	5,190,000	5,503,000
Creosote, etc.	2,093,000	2,963,000
Other coal-tar products	1,174,000	1,496,000
Coal-tar dyes	1,022,000	895,000
Other dyes	544,000	527,000
Barium sulfate	15,000	100,000
White lead	2,950,000	2,526,000
Zinc oxide	294,000	275,000
Other pigments	12,927,000	13,546,000

## ELECTRIC CURRENTS IN CONCRETE

The question of the effect of electric currents in concrete and ferro-concrete, of so much importance now, has been investigated experimentally abroad. Among the more recent researches, according to *The Engineer* (London), 97 (1914), 224, are those undertaken in 1912 by Dr. Müller at the Technical High School of Darmstadt, on behalf of the Deutsche Ausschuss für Eisenbeton, and the similar experiments made last year by Dr. Kurt Lubowsky at the Technical High School of Danzig, and described in the *Elektrotechnische Zeitschrift* of January 1 and 8, 1914.

Lubowsky experimented with prismatic blocks, 12 cm. (4.7 in.) square, 25 cm. (10 in.) high, of various concrete mixtures, some inlaid with iron, which always remained within the blocks covered by 2.5 cm. (1 in.) of concrete. The electrodes were perforated sheets of iron, 7 cm. by 11 cm. by 1 mm. thick, joined to copper leads. The continuous currents were taken from the 220-volt mains, the alternating currents from generators at 60 periods (maximum), and a transformer. The concrete blocks were stored in air or in water. During the setting of the concrete the resistance in the dry increased slowly at first, then more rapidly to 16,000 ohms and more, the rate depending upon the weather. Blocks lying in water increased in weight by absorption of water, while the resistance went quickly down in eight hours from 2200 ohms to about 200 ohms, and remained at that value; the concrete had been allowed to set properly for many days before being immersed in water. When alternating currents were used with wet cement, the drying effect (produced by the heating) raised the resistance.

The results of the electrolytic corrosion tests on the whole agreed with previous tests; in some cases corrosion was observed with continuous currents of lower intensity than is sometimes assumed; occasionally efflorescences of hydroxides of aluminum and iron were noticed. The usual effect is, of course, that the iron is oxidized, swells and cracks the concrete, to which moisture thus gains access. With alternating current wet concrete prisms lying in water absorbed, at first, currents up to 1.5 amperes, but the temperature rose in the course of days to 104° C. within the blocks (as measured by embedded thermometers), while the water temperature did not exceed 42°. After 81 days these blocks were still found in good and strong condition, though the bare-iron electrodes, treated with the same alternating current, began to corrode.

Particular interest attaches to the high-tension experiments. The respective prism was placed on an earthed plate, and another iron plate, joined to a transformer, was put on top of the prism. When currents of 11,000 volts and 0.22 ampere were applied, jets of steam were seen to issue from the block, after two hours, and the jets soon turned into arcs up to 6 cm. in length; some of these arcs fused the concrete, which finally split.

These blocks did not contain any iron. When another block containing a spiral core of iron wire (this wire not being earthed) was similarly exposed to 200,000 volts, the discharge did not pass through the concrete, but a spark or arc would appear somewhere and strike through the air to the earthed plate. It is hence suggested that the lightning-conductors in ferro-concrete structures should be arranged without regard to the iron embedded in the concrete, which cannot well be joined to the conductor network.

Some experiments were finally made on the insulating power of concrete. For this purpose blocks with wire spirals embedded in them were again used. On the block rested a bell insulator, supplied by the Porzellanfabrik Hermsdorf, to which a conductor 1 cm. in thickness was attached, which was connected with a 60,000-volt transformer. The concrete prism stood on an earthed plate, and a voltmeter was inserted between the upper extremity of the wire spiral (which projected out of the concrete in this case) and the earth. The path from the conductor to the earth was thus: bell insulator, concrete, iron spiral, concrete, metal base, and earth. Under these conditions the iron spiral would acquire a potential against the earth which would depend upon the capacity of the bell insulator and the condition and thickness of the concrete layer. The potential difference of the wire spiral rose to 300 volts. This potential might be dangerous to people touching the concrete, provided the current intensity were sufficient. But assuming transformer currents of 100,000 volts at 50 periods, the bell insulators would not allow more than 0.63 milliamperes to pass, while currents of less than 20 milliamperes are not considered dangerous. From



this point of view blocks or columns of ferro-concrete might be used in insulating stands for high-tension insulators. Whether it is advisable to use the iron embedded in the concrete for the purpose of earthing such stands is another question. There might be mechanical damage by perforation of the concrete, though there would hardly be any electrolytic corrosion with high-tension alternating currents.

### TEMPERATURE REGULATOR

A new tank temperature regulator is now offered under the trade name The "Sarco" Regulator. It is easily installed and can be arranged to regulate the temperature of water or any other liquid.

The internal construction of the apparatus is clearly shown in the cut. The thermostatic element "A" is a tubular receptacle containing a heavy hydrocarbon oil into which is inserted a piece of corrugated copper tubing, the length of which is extended or reduced by turning the regulator head "C."

From this thermostatic element a piece of fine copper tubing "D" passes to the controller "G," which also contains a piece of corrugated tubing capable of compression when an

increase of temperature causes the surrounding liquid in "A" to expand. It will be observed, that the thermostatic element "A," the connecting copper tube "D" and the controller "G" form one hermetically closed chamber. When temperature increases in "A" the pressure increases and is transmitted to "G," causing a compression of the copper tube "F," which forces out the piston "I" and tends to close the valve. Spiral springs "E" and "J" operating in the opposite direction tend to keep the valve open.

Regulators can be furnished for the following ranges of temperature: 86-212° F., 140-212° F. and 176-212° F., and others by special arrangement.

The same thermostatic principle has been applied also to room temperature regulator and to a mixing valve which makes possible a continuous discharge of water at a constant temperature.

### STEAM RAISING BY GAS COKE

The *Journal of Gas Lighting and Water Supply*, 125 (1914), 424, publishes some data on steam raising by gas coke, based on evaporation tests officially conducted, under the direction of the London Coke Committee, on boilers at an important municipal pumping-station near London.

The boilers are the ordinary Cornish type, and the full normal evaporative capacity was maintained during the tests without alteration of the existing furnaces or draught conditions. Ordinary

medium-sized gas coke was fired exclusively during the tests, at intervals of 30 to 40 minutes. The competing fuel was smokeless Welsh coal, which was usually stoked at intervals of about 20 minutes. The results obtained demonstrate the comparatively high efficiency of gas coke as a steam-raising fuel, and its adaptability to existing conditions. The feed-water test-meter had been previously checked, and was correctly calibrated within fine limits. The coke fuel was weighed in small lots immediately before firing. Intervals of 1½ hours were allowed in order to establish coke-fires prior to the commencement of the tests, which were twice repeated with similar results. The draught (natural) available was 0.125 inch at the furnace doors.

Duration of tests	4	hours
Steam pressure—Maximum	103.0	lbs.
Minimum	101.0	"
Mean	101.5	"
Feed temperature, average	175°	F.
Total coke fired	1,680.0	lbs.
Average per square foot of grate per hour	12.7	"
Total water evaporated	16,170.0	"
Water evaporated per pound of coke, actual	9.620	"
Factor of evaporation	1.078	"
Water evaporated per pound of coke as fired from and at 212° F.	10.370	"

Commenting on these figures, the *Journal* says: "Though gas coke is now being used extensively on all types of boilers in London, the Committee's experience is that the efficiency of this fuel for steam-raising purposes is little understood by engineers in charge of boiler plants; and it is hoped that the above authenticated test figures may prove useful in dissipating prejudice and in extending the use of gas coke fuel for industrial purposes."

### ENGINEERING REPORT ON ARGENTINE PETROLEUM

Some time ago the Argentine Government appointed an engineer, to supervise the borings on the State reserves of Comodoro Rivadavia. According to the Buenos Aires correspondent of the *Berliner Tageblatt* the engineer has now presented a first report on the subject. It characterizes the depth of an average of 1770 feet at which petroleum has been bored as favorable, especially when it is considered that many very productive and remunerative deposits in other countries have to be pumped up from a depth of from 4000-5600 ft. The productivity of 100 tons daily at first and of from 20 tons to 25 tons later of the individual bore holes at Comodoro Rivadavia leads to the conclusion that there is a possibility of working for many years. The Roumanian sources lie at a depth of 2600 ft. and yield only 10 to 15 tons daily. Nothing definite can yet be stated as to the extent of the Argentine deposits. The geological investigations which have been undertaken seem to prove that the petroleum layers are situated in a stratum about 5 miles long and a few miles wide, which extends toward the Atlantic coast. It is assumed that deposits of bitumen exist in association with the oil, as certain gases and chemical substances have been found in the petroleum which would be able to yield important by-products on rational exploitation.

The report proceeds to remark that it can not yet be stated whether the expectations which have been raised will be fulfilled or, possibly, surpassed, until it is seen whether the sources of petroleum first bored in south Argentina only represent, as usual, the first of several superimposed layers or not. \*\*\* The report suggests that the work should not be proceeded with too hastily, and that private capital as far as possible should be kept at a distance or be so controlled by the Government that the greatest profit is not allowed to be extracted within the shortest possible time, as this practice in other places has resulted in the waste of up to 70 per cent of the possible production of oil.

## NOTES AND CORRESPONDENCE

### THE USE OF OZONE IN VENTILATION<sup>1</sup>

By LUDWIG VON KUPFFER, of BERLIN

It is my purpose to present detailed reports on the present status of ozonization of air for ventilation. The statement of some persons that the engineering profession would never have thought of using ozone had it not been for an exaggerated idea of the physiological benefits of breathing ozone is false, as will be proven on regarding the history of the technical development of the ozone question.

When the ozonization of drinking water had become widespread, the industries realized "that the direct breathing of ozonized air in itself was an insignificant fact, while on the other hand the ozone percentage in the air was of great importance, as it certified to a certain purity of the atmosphere." It was thought that the ozone apparatus used for sterilization of drinking water could not be used for ventilation purposes, and the manufacturers set to work and constructed new types. Practical tests were then made to show that ozone, even in small percentages, was able to purify the air by removing, or at least by lessening, bad odors. I would call attention to the experiments by Dr. Lübbert in Hamburg, made in the hold of the steamer of an ocean-going vessel, which experiments marked an epoch in this question. This was in 1907 and was reported in *Gesundheits Ingenieur*. Lübbert's results were, of course, attacked by various other scientists, but nevertheless, the fact remains that he succeeded in showing that it was possible to reduce bad odors by ozone and thus make the air in an enclosed space bearable. The theoretical discussion in Lübbert's reports is immaterial; what interests the engineer is the practical fact that bad odors caused by human respiratory and life processes can be influenced by ozone so that their disagreeable consequences are eliminated.

The Congress for Heating and Ventilating in Frankfurt (1910) was the first one to spend some time on the question of ventilation with ozone. Engineer Cramer gave a synopsis of the work done to that time on the problem. Cramer stated that an ozonization plant would never be able to take the place of a ventilating plant, but it would be able to be an efficient aid in ventilation. Engineers acquainted with both branches of the industry will know that a combination of ventilating and ozonization plant does not lead to a curtailing of the ventilating plant, but it is clear that such places as the vaults of banks, public baths, and industrial plants would be able to eliminate the too frequent changes of air if they were to combine their ventilating plant with an ozonization plant.

Experience shows that ozone ventilation has two very important points which recommend its use everywhere. These are: first, *the influence on odors*; second, *the purely physiological effects*. This report is merely to cover actual experiences and is not to discuss theoretical questions. There will be no discussion as to whether ozone merely covers up odors, or oxidizes them. The personal ideas of the author were laid down in *Ges. Ing.*, 1913, No. 16, in an article entitled "Improving the Air in Baths by Means of Ozone." The fact remains that the introduction of ozonized air in a room filled with stuffy air brings relief, not only to the people in the room but to others when they enter the room. This is especially clear when a person enters a crowded room from the outside before and after the use of the ozonized air. After a few minutes there is a marked difference in the atmosphere in the room, which is plainly discernible. Years ago experiments were made in a Berlin theatre on a Sunday afternoon, when the theatre was crowded, and it was possible to create a pleasant atmosphere in the theatre within 40 minutes,

in spite of the fact that all windows, ventilators, and exits were closed. The management used ozone between the acts and found, to its satisfaction, that the cases of fainting that had been regular every Sunday disappeared entirely. The influence of ozonized air is especially great upon the respiratory excretions and odors coming from the mouth and nostrils. These odors are prevalent where there is much smoking in a closed room. The stale tobacco smell is strongly influenced by the ozone. Professor Rietschel made detailed investigations in this subject when the Reichstagshaus (House of Commons) was to be equipped with an ozone plant. He recommended the introduction of ozonized air to the great recreation room in the building, as the original ozonators were not able to introduce enough ozonized air to do away with the disagreeable restaurant odors. The result was satisfactory, as is shown by the quotation from Director Jungheim, of the Reichstag: "In answer to your letter of the 15th of May, 1913, I would say that the ozonator plant in the Reichstag works to complete satisfaction, and that the smell from the restaurant, as also the disagreeable odor from smoking tobacco, has almost entirely disappeared."

The observation has been made that it takes time before the odors disappear. That is because inherent odors are very tenacious in rooms. All materials, however, absorb the ozone odor quickly and readily. The obnoxious odors disappear and give place to the fresh odor of ozone, which reminds one of freshly bleached wash. With a longer use of ozone in moderate strength the action takes longer, but lasts longer, and the ozone will continuously eliminate the bad odors, as in the Reichstag, where the restaurant ozone plant is used only for one hour a day. The same influence was observed in the vaults of banks where the ozone offset the strong smell of newly laid linoleum. I cannot agree with my colleague when he states that the inherent odors must be first driven out of the materials, walls, etc., before they can be effectively eliminated by ozone. I would like to use the word "counterabsorption" for this influence of ozone, showing that the bad odors give way to the odors of ozone. Peculiar and of great importance are the disagreeable mixed odors during the first few days. The belief that these "mixed odors" were ozone has often led to mistakes which have played an important role in judging the value of ozone for ventilation. Where there are numerous odors found in new buildings it is advisable to let the ozone apparatus work a few hours before and after working hours, when nobody is in the buildings. If this is done it will not be necessary to use the ozone plant during working hours until the mixed odors have been eliminated. I have numerous opinions from private people who have been in a position to observe ozone plants for years and who know their working from A to Z. In these reports you will hear from physicians who state that the influence of ozone has almost entirely eliminated the odors of sickrooms; you will hear from abattoir managers and veterinarians, who say that the bad air in the dispensaries and abattoirs have been improved; you will hear from bank directors, who bear witness to the excellent influence of ozone on the air in their safe deposit vaults.

Architect Bielenberg, who has had much occasion to notice the influence of ozone on room air, says: "A properly installed and well regulated ozone plant, according to my opinion, adds much to the improvement of the air; it improves the general state of health of the people in the rooms and increases the working capacity of the individual."

The question of how much influence the weakly ozonized air used for ventilation purposes has on the bacteria in the air is of little importance at the present time. Nevertheless, we cannot dismiss the question, for it is here that the contrast between theory and practice seems to be the strongest, for in regard to

<sup>1</sup> Address by Ludwig von Kupfer, of Berlin, at the 9th Congress for Heating and Ventilating, Cologne, Germany, June, 1913. Abstracted by Dr. M. W. Franklin from *Gesundheits Ingenieur*, Aug. 16, 1913, pp. 605-615.

air purification or air improvement we find the greatest difference in opinion as regards the question whether ozone is really able to purify the air, or whether it only covers up the odors; whether, therefore, ozone ventilation is effective or not. Scientific investigations have shown that ozone has no influence on dry bacteria and on the other hand actual practice furnishes us with proofs that even very weakly ozonized air is able to retard the growth of bacteria of putrefaction and of fungus growths. Here we have an antithesis between laboratory results and practical results. Ozonized air is very important in the ventilation of abattoirs and cold storage plants and its adoption in many of these plants is for the very reason that it retards the growth of bacteria, a fact which sanitary engineers grant. We have on the one side the results of Ohlmüller, showing that ozone cannot kill dry bacteria, and on the other hand, practical results show that ozonized air has a retarding influence on their growth. We can explain this contradiction only by some indirect influence, perhaps due to some oxidizing or chemical process acting upon the soil on which these bacteria grow. This chemical change in the soil would be equivalent to a withdrawal of food supply, through which both the growth and the power of reproduction of the bacteria are retarded. This problem has some interest, for if we are able to prevent the growth of germs, or in other words, prevent the formation of soil for their growth by means of ozonized air, we should do so.

I can speak briefly on the question of the poisonous nature of ozone and its supposed harmful effect. Prof. Czaplewski<sup>1</sup> has given detailed information on this point. The practical engineer knows and knew years ago, when there was no question as regards the poisonous nature of ozone, that too large quantities of ozone are harmful. However, even heavily concentrated ozonized air is bearable, though, with difficulty, and has no influence on health. There are men here in this congress who have been in contact with heavily concentrated ozonized air without having suffered in their health. Moreover, Dr. Erlwein shows that the laboratory tests showing the harmful nature of ozone were made with concentrations which were 200 to 1000 times as great as those used for ventilating purposes. The report of Prof. Czaplewski shows that we must differentiate carefully between highly concentrated and weakly concentrated ozonized air. For ventilating purposes the weakly concentrated ozonized air alone need be considered. The limit of concentration in practice is 0.3 mg. per cbm. For pure ventilating plants we rarely use concentrations above 0.09 mg. That these weak concentrations that are hardly perceptible to the senses are still beneficial for ventilating purposes is an assured fact brought out by practical tests.

The oft-occurring statement that ozone can not have a destructive effect on impurities in the air, when used in such small quantities, does not seem to have been proved even by the numerous exact tests. We have to deal, as Prof. Czaplewski says, with very different excretions; some known, some unknown, some complex, others easily volatilized. The tests with only known odors seem in most cases to show a direct influence of ozone. These tests (hydrogen sulfide, skatole, indole, merkap-tane) were made with quantities which could be measured. Consequently, we have a very important use of ozone. It is probably immaterial, as far as the effect is concerned, whether measurable quantities, like 0.1 g. ozone and 0.001 g. skatole; or 0.1 mg. ozone and 0.001 mg. skatole, which latter can not be accurately measured, react on each other. It is well known that many odors, which quantitatively can not be found in the air, have an effect on our senses and are obnoxious. I think it therefore extremely probable that small quantities of ozone have a beneficial effect on these small quantities of obnoxious odors, especially when it is a question of those very volatile and, chemically, partly unknown odors. Only in this way can we reconcile

the statement made by Prof. Bail, of Prague, and of Prof. Goltz, of Berlin, that putrefaction odors and fecal odors are reduced with even small quantities of ozonized air acting upon them, while others claim that ozone could influence these odors only in abnormally large quantities. Ozone concentrations above 1 mg. per 1 cbm. do not come into consideration in practice. No matter how interesting may be the tests made with animals, they have no importance for the ventilating engineer. The ozone industry agrees with Prof. Czaplewski that in ozone ventilation ozone should be used that is entirely free of nitrogen. Konrich used a so-called lattice (grate) apparatus which was only cooled by the air passing through it. The electrode grate acts often as a dust catcher; the very fine dust particles gradually burn, whereby nitrogenous gases may form in small quantities. How far Konrich took account of these points is not known. It is my opinion that my colleague overestimates the danger of the nitrogenous gases in the use of ozone; the small quantities of these gases which an ozone apparatus forms are in no relation to the quantities formed by a single arc lamp per hour and are of course infinitely small related to the total quantities of fresh air in the rooms. With tests on such a small scale as made by Konrich, the relation between air, ozone and nitrogen gases no doubt might be significant.

In practice we follow these points: Weak concentration, good regulation and minute distribution are fundamental requirements for a safe but also an efficient plant. In order to prevent the formation of nitrous acid the plant should be kept clean. Attention should be paid to the formation of mixed odors, especially in new buildings, as was mentioned before. The duration of operation will depend on the different conditions. There should never be use of the ozonator plant without accompanying use of the ventilating plant, otherwise the ratio of mixing will be changed and the effect changed. The usual concentration of ozone in practical operation is not measurable with even the best measuring instruments without slight errors. Nevertheless, the strength of concentration, which is the product of the ventilator capacity and the ozonator capacity, is easily determined. As it is my intention to report on the practical results obtained in actual practice, I have obtained testimonials reaching over a long period of time. The ozonators in these different plants are made by various firms, whose names are of course not mentioned. The letters here given show that the ozonators have met with success in operation.

#### DEODORIZATION BY MEANS OF OZONE

Hamburg, May 31, 1913

Building Department, Section 1, Dept. of Street Cleaning and Refuse Disposal

The employees' sheds at the two refuse incineration plants at the Alte Teichweg and at the Bullerdeich have been equipped with ozone plants. These sheds consist of a locker room, provided for the dirty and filthy clothes, and one for the clean clothing. Both rooms are connected by shower baths and tub baths. The clothes are hung up in these rooms by means of special suspended cords at such a height that they cannot be reached from below. The rooms are ventilated from the ceiling and heated by pipes running along the roof. The room for the dirty clothes is also provided with pure ozone through pipes running parallel at the height of the clothing. . . . . The blower passes the air into these tubes. The ozone plant is started up about one hour before change of shifts and remains in operation until two hours after change. Measurements as regards the quantity of ozonized air per time unit, the ozone percentage of the air, or the ozone percentage of the air between the clothes have not been made as yet. About 1/2 hour after starting up the plant the typical ozone smell is perceptible. THE USUAL ODOR OF PERSPIRATION AND DECAYED REFUSE COMING FROM THESE CLOTHES HAS BEEN SUCCESSFULLY ELIMINATED BY THE OZONATOR PLANT.

May 6 1913

Municipal Market Management, Hamburg

The ozonization plant finds general approval. Our municipal market is a veritable hothouse. The walls are made of glass and iron and the roof is zinc covered. In summer there is usually an unbearable heat, and with large crowds, especially on Saturdays, the air was very bad, due chiefly to the presence of so many people and the great quantities of perishable products, many of them of strong smells. This has been diminished entirely

<sup>1</sup> See *Mit. Chem. Eng.*, 12 (1914), No. 4.



Of course, I have the ozone apparatus work day and night uninterruptedly in the summer, at least during the hottest time. The ozone smell has, however, not shown at all or else only to a very minute extent. WITH CEASING THE OPERATION OF THE OZONATOR PLANT THERE OCCURS VERY SOON A DISTINCT VITIATION OF THE AIR. The public also pays its compliments to the plant, so that I believe I am on the right track when I say that the ozone plant is a necessary adjunct for municipal markets and similar great public halls.

(Signed) VON GLADIS (Manager)

Hamburg, April 6, 1913

Carl Lippmann & Co.

We have had an ozone ventilation installation for about two years and can say that the same works without a hitch in our business, which is connected with RATHER STRONG ODORS, and has proved to be an absolute necessity.

Berlin, May 24, 1913

The Management of the Municipal Abattoir and Shambles

The ozonator plant installed in May, 1911, for the abattoir has proved to be a success. Even though it is not possible to obtain a complete deodorization of the air in the building in which the entrails are reduced, due to the nature of the work itself, nevertheless, the ozonator plant has resulted in a CONSIDERABLE REDUCTION OF THESE NOXIOUS ODORS. Harmful influences on the health of the employees, due to the ozone, have not been noticed in the plant.

(Signed) GOLZ

Complaints by the neighborhood to the odors from this plant have stopped since the plant was installed in 1911.

#### OZONE APPARATUS IN INDUSTRIAL PLANTS

June 6, 1913

Emil Gminder, Reutlingen

My firm, Ulrich Gminder, has had several ozone plants in operation for a number of years. In the cotton spinning and weaving mills where are always found a large number of people and where some of the materials give forth a peculiar odor, there has always been very poor air. The air is bad with ordinary ventilation, WHILE WITH OZONIZATION OF THE AIR WE FIND THE AIR TO BE PLEASANT. Similar plants have been installed with the same success in the big dressing rooms, the offices and other parts of the plants. The effect of the ozone is felt to be especially beneficial in that part of the mill where the fibres in the web are singed off by means of the gas flame. During the years that I have been able to study our ozone plant I have reached the conclusion that ozonization of air is advantageous for all rooms, as long as it is not used to excess, *i. e.*, that the ozone is either not at all noticed or only very slightly.

(Signed) EMIL GMINDER

Rudolf Meidinger, Reichenbach

The ozonization of the air on the whole is felt to be pleasant. The heavy, sultry air gives place to refreshing air. This I have been able to notice only within the last few weeks, when the ozone plant was not in operation, due to the breakdown of one of the motors. The textile industry working the cotton is forced to humidify the air, consequently the work rooms are liable to have a warm, heavy, almost tropical atmosphere, in spite of good ventilation. The capacity for work suffers of course greatly under this. I was therefore very much gratified last week when the ozone apparatus resumed work again. Breathing and respiring, as also the life processes, seem to go on much easier in ozonized air, so that one does not feel the disagreeableness of the hot air. WITH THE INTRODUCTION OF THE OZONIZED AIR IT WAS MORE APPARENT EACH DAY HOW THE DISAGREEABLE ODORS DISAPPEARED. Today there is no trace of these odors. One of the sheds had always had fungi-like growths on the ceiling. These have disappeared since the use of ozonized air, after frequent unsuccessful attempts had been made previously to remove these growths by means of copper sulfate and calcining.

There always used to be a number of workmen who were constantly troubled with diseases of the respiratory organs. These diseases have been reduced. While they used to form the majority of all those on the sicklist, they are now the minority of causes given by the sick people.

(Signed) R. MEIDINGER

May 24, 1913

Municipal, Gas, Water, Electric Works, Heidelberg

In answer to your question of the 16th inst., I would say that the ozonization plant installed in the local public baths has proved successful. It was a question here to remove the bath odor usually found in baths. The ozone was to be a deodorizer in the first place. Great care must be taken in regulating the percentage of ozone. At first too much ozone was admitted and the bathers complained about headaches due to the smell of ozone. The ozone percentage was then reduced and worked satisfactorily. The ozone odor should not prevail.

(Signed) KUKUCK (Director)

#### REPORTS OF PHYSICIANS IN HOSPITALS

June 6, 1913

Royal Sanatorium, Winnental

Answering your question of the 4th inst., I will gladly assert that we are well satisfied with success of the ozonator plant installed in one of the wards. There are no scientific facts as to their influence on the properties of the air. From practical observations, however, we can state that there have been no disagreeable influences, that the insane have never noticed the smell of ozone, AND THAT IN THOSE WARDS WHERE THERE WERE INSANE PATIENTS GIVEN TO UNCLEAN HABITS, THE AIR HAS BECOME CLEANER AND PURER THAN BEFORE. The effect was especially gratifying when the outside temperatures were either very high or very low, as it obviated ventilation by means of opening of windows and exposing the patients to sudden draughts.

(Signed) DR. KREUSER

Karl-Olga Hospital, Stuttgart

June 13, 1913

The ozone ventilation plant has been in operation for three years and gives complete satisfaction. It has a strong, deodorizing effect on the wards in the hospital. THIS WAS SPECIALLY APPARENT WHEN THE PLANT HAD TO STOP FOR SEVERAL WEEKS TO MAKE SOME NEEDED REPAIRS. During this time there was much trouble due to bad odors in the wards. No harmful effect from ozone was noticed, either in patients or in attendants.

(Signed) DR. V. HOFMEISTER

Municipal Katherine Hospital, Stuttgart

June 11, 1913

Answering your question in regard to our ozone apparatus, I can say this: We use a portable plant which we use in places where the natural ventilation is ineffective, or else in rooms where there have been patients with diseases that left a bad odor behind them. For the latter purpose especially, the ozonator proved to be excellent. I was unable, however, to state that the same had a favorable influence on disease processes, combined with putrefactive processes, especially in the lungs, due to the breathing of air containing ozone. THE PATIENTS WHO WERE FORCED TO LIE NEAR PATIENTS WHOSE DISEASES BROUGHT WITH THEM ODOROUS DISCHARGES HAVE ALWAYS ADMITTED THAT THEY WERE VERY GRATEFUL FOR THE EFFECTS PRODUCED BY THE OZONATOR.

(Signed) DR. SICK

Stuttgart Royal Theatre

June, 1913

I have mentioned my ideas as to the value of the ozonators some years ago and still adhere to the same opinions, which are strengthened by facts found by long operation of these ozone plants. With the exception of the vacations, the ozonators in the theatre work every day. THERE IS NO DOUBT THAT THE OZONATOR IS A GREAT BENEFIT TO THE THEATRE PUBLIC. It also reduces the dust. I have made experiments in dressing rooms and toilet rooms, and have found the same to be the case. As regards harmful influences due to breathing the ozone, it seems to me that only gross abuse of the apparatus can have such an effect.

(Signed) DR. GUSMANN

#### OZONE IN ROOMS AND BUILDINGS UNDER NORMAL CONDITIONS

Deutsche Bank, Hamburg

May 30, 1913

Those of our employees who notice the presence of the ozone state that the air has been improved and that it is not as close and stagnated as previously. They say they feel refreshed and improved. The same state also that they miss the ozone if it is not distributed properly by the great ventilating shaft system used there. They say also that at times they have felt unpleasant, when the ozone percentage was too high.

Dresden Bank, Hamburg

May 28, 1913

The ozone plant installed here works to complete satisfaction and the complaints made in the past by employees in regard to poor air have stopped since the operation of the plant.

There follow a few reports from cold storage plants, which bear on the matter of meat and food preservation. Director Klapp, of the Potsdam abattoir, one of the experts on ozone apparatus, writes:

The ozone plant has been in operation in the abattoir for three years. During this time there has been no interruption in service nor any facts that might lead to the conclusion that the ozone has a bad influence on the employees working in the plant. ON THE CONTRARY, THE EMPLOYEES ALL LAUD THE BENEFICIAL EFFECTS OF THE OZONE PLANT. The fact that the butchers' union has recommended the introduction of ozone plants in all abattoirs seems to be an excellent indicator of the feeling of the employees in this regard. Aside from the report made at the last congress on the bacteria contents in the air and the excellent preservation of the beef, we have the tests made last year as regards length of preservation of meats. (Follows a longer report not quoted.)

Director Geiss, of the Straubing abattoir, says as follows:

As far as I am concerned, I may say that the ozone plant, which has been working since 1911, is in excellent condition and satisfactory in every

respect. With the aid of the ozonators we were able, last fall, to preserve beef for 55 days without any decay in the meat. Any odors that occur are removed within five to ten minutes by the ozonator. Such odors appear after holidays, as the ozonators are used only a very short time on the holidays proper.

Unfortunately, time does not permit me to exhaust this almost inexhaustible field. You may draw your conclusions from what I said. One thing you must admit and conclude, namely: that the ozone industry is not bringing a new apparatus on the market in a thoughtless way, bent only on its own profits. Rather we have found that the ozone industry, in view of the practical results obtained and the many inquiries, was justified in following up this line of experiments and in carrying on and exploiting, a process which seemed good and useful to industry. The ozone industry, moreover, will be able to adhere to this viewpoint without fear and doubt.

#### OPERATIONS OF STEEL MILLS IN MARCH

During March, the steel mills throughout the country continued to operate at an average rate of about 75 per cent of capacity, although the rate in the Pittsburgh district was estimated at about 80 per cent. Pig iron production was at a rate slightly above 26,000,000 tons a year. New business came in at a very low rate during the first fortnight of the month; this was attributed to the weather conditions, but there was disappointment that the lull which naturally followed the January buying movement, and which was more or less expected, had not yielded to more active market conditions by the middle of the month. The sheet mills are now operating at an average of about 85 per cent of capacity, while the tip plate mills are operating substantially full. In wire products and tubular goods the conditions are nearly as good.

W. A. HAMOR

#### A RAPID METHOD FOR CASEIN IN MILK—CORRECTION

In THIS JOURNAL, 6, 131, the following paragraph should have been inserted at the end of the article under the above title:

"Since the above work was completed it has been found that beechwood creosote serves as an admirable preservative for milk. When added in the proportion of 5 cc. to 1 pint of milk, the latter keeps in good condition for several months if placed in the dark. The preservative does not interfere with the casein test, nor with the Babcock fat test, provided only one-half the usual amount of sulfuric acid is used."

GORDON HALL OF CHEMISTRY  
SCHOOL OF MINING, KINGSTON, ONTARIO

W. O. WALKER

#### AMERICAN ALCOHOL INSOLUBLE TEST FOR SHELLAC—NOTE

In the method we have described for the determination of the alcohol insoluble matter in lac, the following statement occurs: "During the extraction the alcohol is kept boiling briskly. The extraction is stopped one hour after the alcohol in the siphon tube has become colorless" [THIS JOURNAL, 5 (1913), 435].

We believe it advisable to further standardize the method at this point and recommend that the rate and time of extraction be kept under precise control. The rate of extraction may be controlled by the use of an electric stove of the Simplex type, 4 1/2 inches in diameter, and using the full current of 2.2 amperes at 110 volts. The volume of methyl alcohol in the flask should be 125 cc. This is in addition to the alcohol required to fill the siphon. The flask should be protected from draughts. Under these conditions the tube will siphon over about 33 times an hour. The condenser should be able to return all the alcohol volatilized during the vigorous boiling of the flask contents, the object being to effect the maximum extraction during the fixed time.

The color is removed by the end of the first hour in practically every case and in order to eliminate any variations due to differences of opinion as to the exact time when the color has disappeared we recommend that the total extraction period be limited to exactly two hours, time being taken from the moment when the first siphon tube of alcohol has passed over.

The methyl alcohol used in this method should be 99.5 per cent, by volume.

#### Signed:

C. T. BRAGG, *Chairman*, Director of Laboratories, Berry Bros., Detroit.

GEORGE E. ASHBY, of John R. Anderson & Co., New York.  
A. C. LANGMUIR, Works Manager, Marx & Rawolle, New York.

PARKER C. MCILHINEY, Consulting Chemist, New York.  
JOHN W. PAISLEY, Chemist, Rogers & Pyatt, New York.

#### Approved:

H. S. CHATFIELD, *Secretary*, United States Shellac Importers' Association.

## PERSONAL NOTES

The Russian minister of public instruction has made a grant of \$50,000 to the St. Petersburg Academy of Sciences to assist a search for radio-active minerals throughout the Russian Empire.

Dr. M. G. Donk, of the Bureau of Chemistry, has been detailed by the Department of Agriculture to cooperate with the Department of Forestry at the Univ. of Idaho in investigations looking to better methods of utilizing mill waste and refining by-products obtained from stumps. The work will be a continuation and extension of experiments carried on for the past three years by Dr. C. H. Shattuck, head of the Department of Forestry at Moscow.

A Better Industrial Relation Exhibit will be held April 18-25th, at 2 West 64th Street, New York City. It will show the devices in modern business which tend to make more harmonious the relations between employer and employee, and to better the conditions of employment. The Business Men's Group of the Society for Ethical Culture has charge of the Exhibit, which will appeal to both employer and employee in the manufacturing trades. There will be special evening lectures by industrial leaders of the country.

The American Electrochemical Society will hold its Spring Meeting in New York City, April 16-18th. The program consists of a Symposium on "Power for Electrochemical Purposes" and papers on "Hydro-electrometallurgical Process." The American Electro-Platers' Society will take part in the discussion of the papers on the latter subject.

The Franklin Institute of the State of Pennsylvania has awarded its Elliott Cresson Gold Medal to Prof. Wolfgang Gaede for his molecular air pump, in consideration of the very great value of this invention for the quick production of vacua beyond those hitherto obtainable.

The Board of Regents of the University of Wisconsin has created an Engineering Experiment Station to be established in the College of Engineering and to have general charge of the testing and research work of the college. The staff will consist of the Dean as Director, the members of the instructional staff in the various departments of the College of Engineering and those fellows, scholars and assistants engaged in experimental and research work. This action transfers the appropriation for research now made for the College of Engineering to the En-

gineering Experiment Station. The publication of experimental results at the station will be in the form of bulletins.

The Bethlehem Steel Co. completed negotiations on March 13th whereby a fleet of ten vessels of 15,000 tons burden each will be built to convey iron ore from Cuba to the U. S. The vessels, which will be built by foreign firms, will cost \$700,000 each and are to be completed early in 1917.

The Section of Western New York of the A. C. S. presented the following program at their March 20th meeting at Buffalo: "Accident Prevention," Walter Wallace; "Treatment of Minor Injuries by the Chemist," Dr. Charles E. Taylor; "First Aid," Dr. W. Lewis Wilson.

The St. Louis Section of the A. C. S. has issued a pamphlet containing its By-Laws and a Directory. The latter gives the name, address and telephone number, Business Specialty, Degree and Training of each member of the Section.

Prof. Wolfgang Ostwald, of the University of Leipzig, was entertained at a dinner at The Chemists' Club, New York on Thursday, March 19th. The banquet was attended by a large number of prominent chemists in and about New York. Dr. Charles F. McKenna, President of the Club, presided and introduced Prof. M. T. Bogert as toastmaster. The speakers of the evening were Jerome Alexander, Charles Baskerville, Alexander Smith, Ellwood Hendrick and C. F. Chandler. The speeches were followed by a happy response on the part of the guest, who expressed his sincere approval of the American people and their hospitality. A notable contribution to the entertainment was a poem by Ellwood Hendrick, which follows:

#### THE COLLOID'S LAMENT

I am a simple colloid,  
The place that I live in  
Is very much restricted, for  
I can not squeeze through skin.

I've neither shape nor figure,  
I am not crystalline  
And this it is that breaks my heart;  
Good Lord, how I repine!

I want to be geometric,  
Have sides and angles true,  
And yet I'm bound as hydrocol  
Or gel to be like glue.

Electrolytes disturb me,  
They nearly drive me mad,  
And usually they knock me down  
Which hurts and makes me sad.

Dialysis deludes me,  
As I have said before  
I'm all shut in while crystalloids  
Find many an open door.

I'm sticky and I'm gummy;  
I am the soul of dirt;  
To be like that and know it too—  
Just think how it must hurt!

I'm scorned and I am hated  
And gen'rally despised.  
Professor Ostwald, stand by me  
And make me civilized!

I want a def'nite figure  
Of any standard shape  
So that I can from this blamed mess  
Eventually escape.

Canada has established a Forest Products Laboratory in connection with McGill University at Montreal, on the lines of the U. S. institution of the same sort at the University of Wisconsin.

Mr. Arthur D. Little has been absent recently from his Boston offices on an extended trip to the Middle West and South.

The Cameron Prize of the University of Edinburgh has been awarded to Prof. Paul Ehrlich in recognition of his discovery of salvarsan and other contributions to medical science.

A reception and dinner in honor of Prof. Ira O. Baker, '74, of the University of Illinois, were given at the Hotel LaSalle, in Chicago, on March 17th. There were about 400 guests and the list of speakers included some of the most prominent engineers of the west. Prof. Baker completes in June, 1914, forty years of active, continuous service as a member of the Faculty of the College of Engineering of the University of Illinois.

The Chemical Engineering Society of the University of Kansas at Lawrence, held their First Annual Chemical Engineers' Day, Feb. 27, 1914. The program was as follows: "Manufacture of Portland Cement" (Illustrated), H. A. Rice, Prof. of Civil Engineering; "Bottled Gas," C. J. Myers, Southwestern Blaugas Co., Kansas City, Mo.; "Softening of Hard Water for Railroads," R. C. Bardwell, Chemist for Missouri Pacific Railway, Kansas City, Mo.; "Opportunities for the Chemist, Particularly in the Bureau of Chemistry," F. W. Liepsner, Chief, U. S. Food and Drug Laboratory, Kansas City, Mo.; "The Work of a Railroad Test Department," H. S. Harriman, Chemist and Engineer of Tests, Union Pacific Railroad, Omaha; "Raw Materials for Soap Making," W. J. Reese, Chemist, Peet Bros., Kansas City, Kan.; "The Gypsum Industry in Kansas," R. A. Henley, Amer. Cement and Plaster Co., Lawrence, Kan.; "Technical Uses of Proteins and Some New Methods Desired by the Manufacturers," E. L. Tague, Prof. of Chemistry, Washburn College, Topeka, Kan.; "Contributions to Science by the U. S. Meat Inspection Laboratories," W. B. Smith, Chief Chemist, U. S. Laboratories, Kansas City, Kan.

It is reported that the Mosser tanneries in Pennsylvania, including those at Mahaffey, Noxen and Newberry have been purchased by the Armour Co. of Chicago. The amount paid for these plants and one located at Parsons, W. Va., is said to be \$1,000,000. The capacity of the tanneries is from 1,500 to 1,600 hides per day.

The Oregon Section of the A. C. S. was addressed at their February meeting by Mr. H. N. Lawrie, Chairman of the Commissioners of the Oregon Bureau of Mines and Geology on "the Activities and Organization of the Bureau.

Dr. Edith Ethel Barnard, Instructor in Chemistry at the University of Chicago, died on March 8th.

The Highway Engineering Department of Columbia University gave the following illustrated lectures during the month of March: "The Principles of Efficiency Engineering Applied to Highway Engineering," Frank B. Gilbreth, Consulting Engineer, New York City; "The Administration of Municipal Public Works," Nelson P. Lewis, Chief Engineer, Board of Estimate and Apportionment, New York City; "The Essential Physical and Chemical Properties of Creosoting Oils for Wood Blocks," C. N. Forrest, Chief Chemist, New York Testing Laboratory, Maurer, N. J.; "Relative Cost of Transportation by Waterways, Railways and Highways," John A. Benschel, New York State Engineer, Albany, N. Y.

The Scientific Materials Company of Pittsburgh announce the establishment of a research department for the special study of laboratory apparatus and research equipment. The laboratory organization is to be entirely independent of the manufacturing and sales departments and is to devote its attention to research problems. The laboratory staff is as follows: E. H. Fisher, Electrical Engineer, *Director*; T. W. Clark, Chemical Engineer; H. W. Gochbauer, Sanitary Engineer; C. G. Fisher,



Mechanical Engineer; J. R. Brueckner, Pyrometric Engineer; R. E. Barlow, Mining Engineer; A. Betzold, Expert Glass Blower; A. Ruckstahl and F. Luchs, Precision Mechanics.

The American Institute of Chemical Engineers will hold its 6th Semi-annual Meeting at Troy, New York, June 17-20, 1914.

The Rochester Section of A. C. S. had as speaker for their March 3rd meeting, Mr. W. R. Hulburt, Sales-manager of the Goldschmidt Thermit Co., whose topic was "The Theory and Practical Application of Thermit." The lecture was elaborately illustrated by laboratory experiments, practical welding demonstrations, lantern slides and motion pictures.

Mr. E. F. Platt, formerly with the Platt Iron Works of Dayton, O. and Mr. C. A. Kurz, Jr., of the Kurz Laboratories, have recently organized the Electrolytic Gas Company. This company has secured the Western selling agency of the International Oxygen Company of New York and it is their intention to proceed with the installation of a number of electrolytic plants of the I. O. C. System for the production of oxygen and hydrogen in different parts of the country.

The Connecticut Valley Section of the A. C. S. met at Springfield on March 2nd. The program was as follows: "Progress in our Knowledge of the Atom," Dr. E. W. Morley; discussions of "Use of Electrical Apparatus in the Laboratory," and "Corrosion of Metal by Water" (THIS JOURNAL, 5, 905).

The Regents of the University of Wisconsin have created 15 industrial scholarships to aid in satisfying the demand for professionally trained mechanics to teach in industrial schools. Each scholarship carries with it a special honorarium of \$40, and the holders of these scholarships are to be organized into a mechanics' institute to be held from March 9th to April 9th, for intensive practice in special lines of shop work and drawing and a detailed consideration of organization and teaching problems that confront industrial schools.

The North Carolina Section of the A. C. S. at their Mid-winter meeting at Raleigh on Jan. 24th, presented the following papers of industrial interest: Presidential Address, "The Engineering Students' Need of Chemistry," L. F. Williams; "The Stability of Resin Acids at Slightly Elevated Temperatures," C. H. Herty and H. L. Cox; "Studies in Nitrification," W. A. Withers and A. L. Field; "Neutral Solutions of Ammonium Citrate," J. M. Bell; "A Volumetric Method for Arsenates," J. M. Bell and A. J. Flume.

Mr. C. F. Woods, of the staff of Arthur D. Little, Inc., on Feb. 6th spoke before the salesmen of the Walter M. Lowney Co., of Boston, upon the general topic of "Pure Food" with its particular bearing upon the manufacture of candy.

Dr. Raymond Foss Bacon has been appointed to succeed the late Prof. Robert Kennedy Duncan as Director of the Mellon Institute for Industrial Research of the University of Pittsburgh. Dr. Bacon was formerly Associate Director of the Institute.

The St. Louis Section of the A. C. S. discussed "Fire Risks in Chemical Factories" and "The Standardization of Weak Solutions" at their March meeting on the 9th.

Prof. Loehnis, of the Laboratory of Agricultural Bacteriology in the University of Leipzig, has accepted the offer of a position in the Department of Agriculture at Washington.

Mr. Maximilian Toch of New York City spoke on "Paint as

an Engineering Material (Illustrated)" before the Philadelphia Section of the A. C. S. on March 19th.

The Nashville Section of the A. C. S. had the following program on March 20th: "Synthetic Rubber," Dr. J. T. McGill; "The Enforcement of the National Food and Drugs Act," Dr. R. W. Balcom.

The Calendar of the Public Lectures in the Department of Chemistry of the College of the City of New York for the Spring Semester, is as follows: Feb. 27th—"Fixation of Nitrogen," Prof. H. R. Moody of the College staff; Mar. 13th—"The Growth of Crystals" (with moving pictures), Mr. S. G. Warner, Physicist in Edison Laboratories; Mar. 20th—"Colloids" (Illustrated), Dr. Wolfgang Ostwald, Univ. of Leipzig; Apr. 3rd—"Municipal Control in the Purchase of Supplies," Dr. Otto H. Klein, Director Standard Testing Laboratories, Board of Estimate and Apportionment, New York City; May 1st—"Some Economic Aspects of Industrial Chemistry," Dr. Bernhard C. Hesse, Chemical Expert and Patent Attorney.

Prof. Heinrich Ries spoke before the Cornell Section of the A. C. S. on "Underground Water Supply" on March 23rd.

Prof. Elton Fulmer, Dean of Washington State College and Head of the Department of Chemistry, and wife were guests of honor at a banquet given by the members of the Chemistry Department and their wives, upon their return from an extended trip through the U. S. and the Hawaiian Islands. Prof. and Mrs. Fulmer gave very interesting talks during the evening—the former on "The Historical Events of the Islands and their Development" and the latter on "The People and their Customs as observed in the Present Period."

The Rochester Section of the A. C. S. have the following lectures scheduled: March 16th, "The Application of Chemistry to the Baking Industry," Mr. David Coford; April 6th, "Metallography," Prof. William Campbell of Columbia University; May 4th, "Our Present Knowledge of Crystals," Prof. Frank Kenrick of the University of Toronto.

Under the new organization of the Food and Drug Inspection work of the Bureau of Chemistry, the chief of each district must send full reports on analyses, hearings and all other matters to the Chief Chemist, and his findings are subject to review at Washington. The district chief, however, cannot institute a prosecution or a seizure, as all cases calling for prosecution or seizure must be first passed upon in Washington by the Chief Chemist who since Feb. 1st does the work formerly done by the Board of Food and Drugs Inspection. The new organization brings about absolute correlation in work and complete coöperation between the inspectors and laboratories and will greatly expedite the handling of samples, holding of hearings and the preliminary disposition of cases.

The International Oxygen Co. entertained the members of the Manufacturing and Sales Departments at a dinner at the Hotel McAlpin, New York City lately. Among those present were: Mr. Solomon Heller, Mr. and Mrs. Samuel Heller, Mr. and Mrs. A. A. Heller, Mr. E. W. Irwin, Mr. I. H. Levin, Mr. and Mrs. H. L. Barnitz, Mr. and Mrs. C. Aichberger, Mr. and Mrs. D. J. Tonkonogy, Miss Celie Weiss, Miss Leona Friedland, Mr. H. W. Timm and Mr. Philip Fried.

Dr. Wolfgang Ostwald lectured on "Colloids" before the Syracuse Section of the A. C. S. on March 18th.

## BOOK REVIEWS

**Der Stärkezucker: Chemische und technologisch behandelt.** VON DR. H. WICHELHAUS, Geh. Reg. Rat, Professor und Direktor des Technologischen Instituts der Universität Berlin. Mit 57 Abbildungen, Leipzig, 1913, Akademische Verlagsgesellschaft.

The present volume fills a long-felt want, since the student and

technologist has now, for the first time, a book which covers all the principal facts relating to the chemistry and manufacture of dextrose. In the preparation of his work the author has availed himself of all possible sources; historical documents, archives of scientific societies, chemical journals, government reports and patent lists have all been consulted and the reader has now, in

one book, information which was hitherto widely scattered and in some cases difficultly available.

The starch-sugar industry, like that of beet sugar, owes its first developments to Napoleon, who first by prohibiting commerce with England shut out colonial products from Europe and then by awarding premiums gave encouragement to the foundation of a continental sugar industry. In 1811 Kirchhoff, member of the Imperial Academy at St. Petersburg, discovered a method for converting starch into dextrose by means of acids and the original account of his process, which the author gives in full, is of great interest.

Carl August, Grand Duke of Weimar (the well known friend of Goethe and Schiller), founded the first stock company for making starch sugar and a factory was organized at Tiefurt in 1812 under the direction of Döbereiner. The overthrow of Napoleon and the abolition of his Continental System, however, reopened the markets of Europe to cane-sugar and put an end to this new enterprise, although the infant beet-sugar industry, through wise governmental support in France, was able to weather the storm.

The next important step in the development of the starch-sugar industry took place in the United States and for the history of what was henceforth to be essentially an American enterprise the author has drawn upon papers by Herstein (*THIS JOURNAL*, 3, 158), Wagner (*J. Soc. Chem. Ind.*, 1909, 345) and others.

The sections of the book devoted to the chemistry of dextrose, processes of manufacture, utilization, analytical methods, etc., are very complete and the subject matter is brought well up to date. The researches of Behr, Rolfe, Duryea, Noyes, and other American investigators are fully presented.

In addition to the manufacture of dextrose from starch, its preparation from cellulose and wood is also considered. The extension of the term starch-sugar to the product derived from other materials than starch is perhaps permissible, when we consider the application of the term cane-sugar to the products of the beet and maple. Such license with the literal meaning of words has caused, however, much misunderstanding, especially in the minds of laymen. In the present case this confusion is increased, owing to the fact that the term starch-sugar is also sometimes given to maltose.

A few slight errors have been noted. The specific rotation of  $\beta$ -glucose is given incorrectly as  $+52.5$  on page 39; it is stated correctly as  $+20.46$  on page 44. The statement on page 31 that "ripe sound sugar cane contains almost exclusively glucose, which soon goes over to saccharose" requires modification. The author probably means that the reducing sugar of very mature sugar cane consists almost exclusively of glucose.

The book is well printed, and as a whole free from typographical errors. We note, however, a few misspelling of names, as Beaumé (p. 11) for Baumé and Dulrunhaut (in the Index) for Dubrunfaut.

The volume is furnished with a good patent list. The author states that there are about 170 American patents on starch-sugar alone; of this number he mentions 70, those before 1882 being omitted as of only historical interest.

A most serious omission in the volume is the lack of a subject index. An index of names is given, but this is inadequate in the search for particular subjects. The price of the book (11 marks unbound) is somewhat above the average for scientific books of this kind.

We recommend this new work of Dr. Wichelhaus to all who are interested in the chemistry of sugar or in the technology of carbohydrates.

C. A. BROWNE

**Natronzellstoff.** By CHRISTIAN CHRISTIANSEN. 154 pp. Publishers, Gebrüder Borntraeger, Berlin.

This monograph, which has received a prize from the Verein der

Zellstoff und Papierchemiker, gives a short, but excellent historical summary of the various processes used for the manufacture of cellulose, of the more recent advances in the technical processes used. It discusses the Kraft method. The theory governing the digestion processes is treated at length and is followed by the most interesting part of the book, the experimental work of the author. This consists of a series of sodium hydroxide digestions, the object of which was to explain the course of the reaction of this process. The author found certain critical points in the soda consumption curve, which showed that the course of the reaction depended not only on the time, temperature and pressure but also on the amount and strength of the caustic solution.

An attempt has also been made to examine the substances obtained in this process as to their chemical constitution. A valuable feature of the book is an extensive chronological table of the patent and journal literature with an abstract of each patent or article.

SIDNEY BORN

**Coast Erosion and Protection.** By ERNST R. MATTHEWS, Assoc. M. Inst., C.E., F.R.S. (Ed.), F.R.G.S., F.G.S. J. B. Lippincott Company, Philadelphia, 1913. Price, \$3.50.

This is a timely work, and one that will no doubt prove a valuable contribution to this important branch of civil engineering. The growth and depletion of sea-beaches as a result of wave action is not only a subject of great interest but is one of those larger questions which affect states and nations. The configuration of some coast lines is not the same for two consecutive days. Low headlands, formed of easily eroded material, are continually being set backwards, owing to the inroads of the sea and accretion takes place very rapidly, so much so, that land is reclaimed in large areas.

The volume under review deals especially with the erosion and accretion that is taking place around the coasts of Great Britain and Ireland but the conditions prevailing there apply equally to the inroads of the sea at many points along the American coast line. The enormous damage to property by wave action during a recent storm along our own New Jersey shore, the destruction of property valued at hundreds of thousands of dollars occurring during a storm lasting a few hours, is but a single example of the necessity of sea-coast protection.

In this work, the author treats of all forms of sea defences, the merits and demerits of each type being fully discussed. Many facts bearing on the comparative value of the different materials suitable for the construction of sea walls are also presented, without losing sight of the important item of economy. Special consideration is given to methods of construction in reinforced concrete and comparisons of costs are stated. An optimistic, though conservative view of the ascendancy of concrete in this type of work is taken. The fact is that no material is used so extensively at the present time, nor likely to be more used in the future in the construction of sea walls and breakwaters.

A carefully written chapter on the action of sea water on concrete summarizes the unsatisfactory state of our knowledge on this vexing subject. The author records in this chapter the results of a series of experiments on a high alumina cement but unfortunately does not give the number of briquettes from which the average strengths were computed, and possibly lays too much significance on the strength tests over short periods, 7, 14 and 28 days.

The book is well bound and printed and admirably illustrated with drawings and photographs. To maritime engineers or those engaged in harbor construction this work will prove a useful acquisition.

RICHARD H. GAINES

# NEW PUBLICATIONS

By D. D. BERGOLZHEIMER, Librarian The Chemists' Club, New York

**Analysis, Chemical, Rays of Positive Electricity and their Application to.** By J. J. THOMSON. 8vo, 129 pp. Price, \$1.25. Longmans, Green & Co., New York.

**Calculations, Chemo-technological.** By FERDINAND FISCHER. 8vo. Price, \$0.75. Otto Spamer, Leipzig. (German.)

**Cement, Concrete and Bricks.** By A. B. SEARLE. Demy 8vo. Price, \$2.75. Constable & Co., London.

**Cement: A Manual for Bricklayers, Concrete Workers and Plasterers.** By J. A. VAN DER KLOES. 8vo. Price, \$2.25. J. & A. Churchill, London.

**Chemistry for Engineers and Manufacturers.** By BERTRAM BLOUNT. Vol. II, 2nd Ed. L. 8vo. Price, \$7.50. Charles Griffin & Co., London.

**Cyanid Compounds, The Industry of the.** By HIPPOLYT KOEHLER. 8vo, 200 pp. Price, \$2.25. Friedrich Vieweg & Sohn, Brunswick. (German.)

**Cyanogen Compounds, The Industry of the, their Development and Present Status.** By HIPPOLYT KOEHLER. 8vo, 200 pp. Price, \$2.00. Friedrich Vieweg & Sohn, Brunswick. (German.)

**Dyeing and Bleaching of Vegetable Fibrous Material, The Chemistry of.** By JULIUS HUEBNER. Demy 8vo. Price, \$3.50. Constable & Co., London.

**American Electrochemical Society, Transactions of the. XXIV.** Editor, J. W. RICHARDS. 8vo, 306 pp. Price, \$2.50. American Electrochemical Society, South Bethlehem, Pa.

**Food Materials, Methods of Examination of.** By A. C. BEYTHIEN, HARTWICK and KLEIMMER. 3 Vols. Lex. 8vo. 1072 pp. Price, \$10.75. Ch. H. Tschunke, Leipzig. (German.)

**Fuel-Briquetting Investigations, July, 1904 to July, 1912.** By C. L. WRIGHT. 8vo, 277 pp. U. S. Bureau of Mines, Bulletin 58.

**Fuel, An Introduction to the Study of.** By F. J. BRISLEE. Demy 8vo. Price, \$2.25. Constable & Co., London.

**Fuel, Solid, Liquid and Gaseous.** By J. S. S. BRAME. 8vo, 367 pp. Price, \$3.25. Edward Arnold, London.

**Gas Reactions, The Physical Chemistry of the Homogeneous and Heterogeneous.** By KARL JELLINEK. I. 8vo, 844 pp. Price, \$8.00. S. Hirzel, Leipzig. (German.)

**Glass Blowing, Laboratory Manual of.** By FRANCIS C. FRARY. 8vo, 60 pp. Price, \$1.00. Hill Publishing Co., London.

**Industry, Chemical and Color.** By CARL C. CHRISTIANSEN. 8vo, 100 pp. Price, \$0.75. J. C. B. Mohr, Tübingen. (German.)

**Inorganic Chemical Industry, Pocketbook for the.** By G. LUNGE and F. KELL. 5th Ed. Sm. 8vo, 305 pp. Price, \$2.00. Julius Springer, Berlin. (German.)

**Inorganic Chemistry, Modern, Introduction to.** By J. W. MELLOR. 8vo, 684 pp. Price, \$1.30. Longmans, Green & Co., New York.

**Inorganic Chemistry, Short Textbook of.** By LOTHAR WOHLER. 8vo, 203 pp. Price, \$1.50. S. Hirzel, Leipzig. (German.)

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## RECENT JOURNAL ARTICLES

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**Boiler Scale, its Cause and Prevention.** By PAUL MARTELL. *Chemische Apparatur*, Vol. 1, 1914, No. 3, pp. 39-41.

**Carnotite Industry, The.** By S. FISCHER. *Transactions of the American Electrochemical Society*, Vol. 24, 1914, pp. 361-375.

**Casein, Its Preparation and Testing for Coated Paper Work.** By E. SUTERMEISTER. *Pulp and Paper Magazine of Canada*, Vol. 12, 1914, No. 5, pp. 126-129.

**Cellulose, Cotton, The Action of Strong Nitric Acid on.** By EDMUND KNECHT and ADOLF LIPSCHUTZ. *Journal of the Society of Chemical Industry*, Vol. 33, 1914, No. 3, pp. 116-122.

**Coal, Analysis of, and Generation of Steam.** By CHAS. L. HUBBARD. *Steam*, Vol. 13, 1914, No. 3, pp. 63-67.

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**Dyeing: Public Report of the Committee on Quality of Dyestuffs.** By CLAIRMONT, et al. *Chemiker Zeitung*, Vol. 38, 1914, No. 15, pp. 154-158.

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**Glasses, Soda-Lime-Silicate, Selenium as Coloring Matter for.** By PIERO FENAROLI. *Chemiker Zeitung*, Vol. 38, 1914, No. 16, pp. 177-180.

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**Iron, Cast, The Influence on Quality of, Exerted by Oxygen, Nitrogen and Some Other Elements.** By J. E. JOHNSON, JR. *Bulletin of the American Institute of Mining Engineers*, 1914, No. 85, pp. 1-40.

**Iron and Steel, Electrometallurgy of.** By WOLSEY MCA. JOHNSON. *Metalurgical and Chemical Engineering*, Vol. 12, 1914, No. 3, pp. 165-168.

**Natural Gas, Its Supply and Distribution for Fuel.** By EVAN RINGHART. *Monthly Bulletin of the Engineers' Club of Baltimore*, Vol. 3, 1914, No. 5, pp. 2-4.

**Oil, Hardened.** By G. MEYERHEIM. *Seifenfabrikant*, Vol. 34, 1914, Nos. 8 and 9, pp. 177-178, 206-208.

**Oil, The Viscosity of.** By J. L. STREUVENS. *Journal of the Society of Chemical Industry*, Vol. 33, 1914, No. 3, pp. 109-111.

**Oil: Scientific Installations for the Economical Burning of Liquid Fuel of any Specific Gravity.** By W. N. BEST. *Bull. of Amer. Inst. of Mining Engineers*, 1914, No. 86, pp. 267-277.

**Peat-tar, Studies on: I. The Phenol of Peat-coke-tar.** By E. BOERNSTEIN and F. BERNSTEIN. *Zeitschrift fuer angewandte Chemie*, Vol. 27, 1914/I, No. 12, pp. 71-72.

**Refractory Elements, Melting Points of the.** By G. K. BRUGGESS and R. G. WALTENBERG. *Bulletin of the Bureau of Standards*, Vol. 10, 1914, No. 1, pp. 79-90.

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**Sodium, The Production of.** By BERNHARD NEUMANN and SIGURD GIERTSEN. *Zeitschrift fuer angewandte Chemie*, Vol. 27, 1914/I, No. 12, pp. 65-70.

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**Wood Pulp in Textile Manufacturing, Utilization of.** By H. A. CARTER. *Pulp and Paper Magazine of Canada*, Vol. 12, 1914, No. 4, pp. 102-105.



# RECENT INVENTIONS

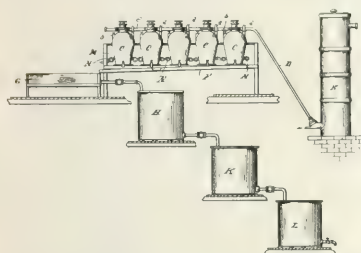
By C. L. PARKER, Solicitor of Chemical Patents, McGill Building, Washington, D. C.

**Catalytic Production of Ammonia.** Bosch and Mittasch, Jan. 6, 1914. U. S. Pat. 1,083,585. Ammonia is produced from its elements by the catalytic action of pure iron, which has been prepared from its compounds by treatment with ammonia at a temperature above 600° C.

**Producing Ammonia and Compounds of Ammonia.** F. Rothe, Jan. 6, 1914. U. S. Pat. 1,083,703. A gaseous mixture containing hydrogen together with compounds of nitrogen and oxygen is passed at a high temperature over a contact mass containing from 1 to 10 per cent of a catalytic substance.

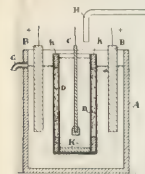
**Producing Hydrogen Peroxid.** Pietzsch and Adolph, Jan. 6, 1914. U. S. Pat. 1,083,888. Hydrogen peroxid is produced by subjecting a mixture of persulfate and sulfuric acid to the action of steam, the steam heating the mixture and reacting directly with it to form hydrogen peroxid vapor.

**Production of Lead Solutions from Lead Ore.** Anderson and Kaar, Jan. 13, 1914. U. S. Pat. 1,083,910. Lead solutions are produced directly from galena by treating the pulverized ore with a 7 per cent solution of nitric acid at a temperature of 150 to 165° F. The oxids of nitrogen are recovered in the form

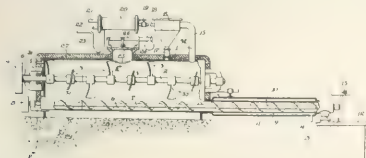


of dilute nitric acid which is mixed with concentrated acid to produce the standard solution for dissolving the lead. The impure lead nitrate solution is purified from iron by precipitating the iron in two successive stages.

**Electrolytic Production of Copper.** N. V. Hybinette, Jan. 13, 1914. U. S. Pat. 1,084,150. Copper is produced direct from the ore by leaching the ore and plating from the resulting solution containing both copper and iron salts by passing it into the cathode compartment of an electrolytic cell and circulating the solution through a filter in the direction from cathode to anode.

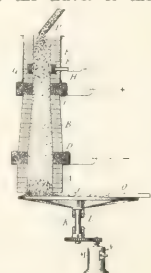


**Preparing Catalysts and Apparatus Therefor.** C. Ellis, Jan. 13, 1914. U. S. Pat. 1,084,202. A charge of catalyst raw material such as charcoal, iron oxid or the oxids of nickel, cobalt, copper, etc., is placed in the treating



chamber 1, and heated to a temperature of from 300° to 500° C. Hydrogen or other reducing gas is introduced by

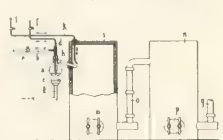
the line of pipe 30 and a portion of the gas passes over the top of the charge while another portion enters beneath the charge. The conveyor 7 is rotated so that the charge is moved downwardly to some extent on the side where the hydrogen enters in the lower part of the conveyor. The mixing conveyor 2, by rotation in an opposite direction, moves the upper strata of material in a direction opposed to that of the travel of the material in the lower part of the chamber. The reduced material is withdrawn without contact with air, cooled and transferred without material oxidation to the place of use.



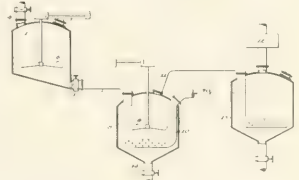
**Graphitizing Carbon.** P. L. T. Héroult, Jan. 13, 1914. U. S. Pat. 1,084,274. In this apparatus the carbon, broken to a suitable size, is subjected to a blast of air under such conditions that it is considerably heated. It is then heated to a graphitizing temperature electrically.

**Mercuric Chlorid and Process of Producing same.** Kaufler

and Klages, Jan. 13, 1914. U. S. Pat. 1,084,346. Chlorin and mercury are separately introduced into a retort containing boiling mercury, the mercury being introduced below the level of the boiling mercury. The mercury bichlorid vapors escaping from the retort are chilled by the use of a large quantity of cold air. The mercury bichlorid produced in this way forms fine voluminous crystallized needles.



**Making Solid Sodium Bisulfite.** H. Howard, Jan. 13, 1914. U. S. Pat. 1,084,436. Sodium sulfite substantially free from sodium carbonate and suspended in a solution containing sodium sulfite is treated with burner gas to convert the suspended sodium sulfite into sodium bisulfite.



**Zirconium Lamp-Filament.** C. A. Hansen, Jan. 20, 1914. U. S. Pat. 1,084,629. Zirconium oxalate is mixed with finely divided carbon. The mixture is shaped into threads and the threads heated to produce refractory filaments consisting essentially of zirconium.

**Obtaining Nitrogen and making Compounds therefrom.** Willson and Haff, Jan. 20, 1914. U. S. Pat. 1,084,774. Nitrogen is obtained from the atmosphere by burning sulfur in a confined body of air and passing the resulting gaseous mixture through a solution containing lime to form bisulfite liquor. The remaining gas is then passed over heated sulfur and the nitrogen collected.

**Method of Carbonizing and Superheating Gas.** A. Berglof, Jan. 20, 1914. U. S. Pat. 1,085,096. The gas to be carbonized and superheated is first preheated and passed through a body of coke maintained incandescent by means of an electric current, out of contact with the air.

# MARKET REPORT

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR THE MONTH OF MARCH, 1914

## ORGANIC CHEMICALS

Acetanilid.....	Lb.	21 1/2	@	23 1/2
Acetic Acid (28 per cent).....	C.	1.50	@	1.65
Acetone (drums).....	Lb.	10 1/2	@	13
Alcohol, denatured (180 proof).....	Gal.	35	@	37
Alcohol, grain (188 proof).....	Gal.	2.52	@	2.54
Alcohol, wood (95 per cent).....	Gal.	45	@	47
Amyl Acetate.....	C.	1.60	@	1.70
Aniline Oil.....	Lb.	10	@	10 1/2
Benzoic Acid.....	Lb.	23	@	27
Benzol (90 per cent).....	Gal.	23	to	25
Camphor (refined in bulk).....	Lb.	42 1/2	@	45
Carbolic Acid (drums).....	Lb.	7 3/4	@	10
Carbon Bisulfide.....	Lb.	6 1/4	@	8
Carbon Tetrachloride (drums).....	Lb.	7 1/4	@	7 1/2
Chloroform.....	Lb.	22	@	32
Citric Acid (domestic), crystals.....	Lb.	51	@	52
Dextrine (corn).....	C.	2.52	@	2.72
Dextrine (imported potato).....	Lb.	5	to	6
Ether (U. S. P., 1900).....	Lb.	18	@	24
Formaldehyde.....	Lb.	8 1/2	@	9 1/2
Glycerine (dynamite).....	Lb.	21	@	21 1/2
Oxalic Acid.....	Lb.	7 1/4	@	7 1/2
Pyrogallie Acid (bulk).....	Lb.	1.20	@	1.40
Salicylic Acid.....	Lb.	25	@	30
Starch (cassava).....	Lb.	3 1/4	@	4
Starch (corn).....	C.	1.84	@	2.50
Starch (potato).....	Lb.	4 1/4	—	4 1/4
Starch (rice).....	Lb.	8	@	9
Starch (sago).....	Lb.	2 1/4	@	2 1/4
Starch (wheat).....	Lb.	5 1/4	@	6 1/2
Tannic Acid (commercial).....	Lb.	35	—	36
Tartaric Acid, crystals.....	Lb.	30 1/2	@	31

## INORGANIC CHEMICALS

Acetate of Lead (brown, broken).....	Lb.	7 1/4	—	7 3/4
Acetate of Lime (gray).....	C.	1.50	@	1.55
Alum (lump).....	C.	1.75	@	2.00
Aluminum Sulfate (high-grade).....	C.	1.25	@	1.75
Ammonium Carbonate, domestic.....	Lb.	8	@	8 1/2
Ammonium Chloride, gray.....	Lb.	5 1/4	@	6 1/4
Aqua Ammonia (drums) 16°.....	Lb.	2 1/4	@	2 1/2
Arsenic, white.....	Lb.	3	@	3 1/4
Barium Chloride.....	C.	1.60	@	1.75
Barium Nitrate.....	Lb.	5	to	5 1/4
Barytes (prime white, foreign).....	Ton	19.00	@	23.50
Bleaching Powder (35 per cent).....	C.	1.20	@	1.30
Blue Vitriol.....	Lb.	4.80	@	5 1/4
Borax, crystals (barys).....	Lb.	3 3/4	@	4 1/2
Boric Acid, crystals (powd.).....	Lb.	7	@	7 1/4
Brimstone (crude, domestic).....	Ton	22.00	@	22.50
Bromine, bulk.....	Lb.	30	@	35
Calcium Chloride, fused.....	C.	57 1/2	@	85
Chalk (light precipitated).....	Lb.	4	@	4 1/2
China Clay (imported).....	Ton	nominal		
Feldspar.....	Ton	8.00	@	12.00
Fuller's Earth, powdered, Foreign.....	Ton	16.00	@	17.00
Green Vitriol (bulk).....	C.	55	@	60
Hydrochloric Acid (18°).....	C.	1.15	@	1.55
Iodine (resublimed).....	C.	3.55	@	3.60
Lead Nitrate.....	Lb.	8	@	8 1/4
Litharge (American).....	Lb.	5 1/2	@	5 3/4
Lithium Carbonate.....	Lb.	65	@	70
Magnesium Carbonate.....	Lb.	21	@	35
Magnetite "Calcinad".....	Ton	28.50	@	29.50
Nitric Acid, 36°.....	Lb.	3 1/4	@	4 1/4
Phosphoric Acid (sp. gr. 1.75).....	Lb.	20	@	24
Phosphorus.....	Lb.	45	@	1.00
Plaster of Paris.....	Bbl.	1.50	@	1.70
Potassium Bichromate, 50°.....	Lb.	6 1/4	@	7
Potassium Bromide.....	Lb.	10	@	40
Potassium Carbonate (calcinad), 80 @ 85%.....	C.	3 1/4	@	3 1/2
Potassium Chlorate, crystals.....	Lb.	7 1/4	@	7 1/2
Potassium Cyanide (bulk), 98-99%.....	Lb.	19	@	22
Potassium Hydroxide.....	C.	4.00	@	4.25
Potassium Iodide (bulk).....	Lb.	2.95	@	3.00
Potassium Nitrate (crude).....	Lb.	4 1/4	@	5 1/4
Potassium Permanganate (bulk).....	Lb.	10	@	10
Quicksilver, Flask (75 lbs.).....	Lb.	8.00	@	8
Red Lead (American).....	Lb.	6	@	6 1/4
Salt Cake (glass-makers').....	C.	55	@	65

Silver Nitrate.....	Oz.	36 1/4	@	38 1/4
Soapstone in bags.....	Ton	10.00	@	12.00
Soda Ash (48 per cent).....	C.	67 1/2	@	72 1/2
Sodium Acetate.....	Lb.	3 3/4	@	4 1/4
Sodium Bicarbonate (domestic).....	C.	1.00	@	1.10
Sodium Bicarbonate (English).....	Lb.	2 1/4	@	3
Sodium Bichromate.....	Lb.	4 1/4	@	4 1/2
Sodium Carbonate (dry).....	C.	60	@	80
Sodium Chlorate.....	Lb.	7 1/4	@	7 1/2
Sodium Hydroxide, 60 per cent.....	C.	1.55	@	1.57 1/2
Sodium Hyposulfite.....	C.	1.30	@	1.60
Sodium Nitrate, 95 per cent, spot.....	C.	—	@	2.22 1/2
Sodium Silicate (liquid).....	C.	65	@	1.50
Strontium Nitrate.....	Lb.	6 1/4	@	7
Sulfur, Flowers (sublimed).....	C.	2.20	@	2.60
Sulfur, Roll.....	C.	1.85	@	2.15
Sulfuric Acid, 60° B.....	C.	85	@	1.00
Talc (Alberca).....	Ton	15.00	@	20.00
Terra Alba (American), No. 1.....	C.	75	@	80
Tin Bichloride (50°).....	Lb.	11 1/4	@	12 1/4
Tin Oxide.....	Lb.	42	@	44
White Lead (American, dry).....	Lb.	5 1/4	@	5 1/2
Zinc Carbonate.....	Lb.	8 1/2	@	9
Zinc Chloride (granulated).....	Lb.	4 1/2	@	5
Zinc Oxide (American process).....	Lb.	5 1/4	@	6 1/4
Zinc Sulfate.....	Lb.	2 1/2	@	3

## OILS, WAXES, ETC.

Beeswax (pure white).....	Lb.	45	@	47
Black Mineral Oil, 29 gravity.....	Gal.	13 1/2	@	14
Castor Oil (No. 3).....	Lb.	8 1/4	@	8 1/2
Ceresin (yellow).....	Lb.	12	@	22
Corn Oil.....	C.	6.45	@	6.60
Cottonseed Oil (crude), f. o. b. mill.....	Gal.	45	@	45 1/2
Cottonseed Oil (p. s. y.).....	Lb.	7 1/4	@	7 3/4
Cylinder Oil (light, filtered).....	Gal.	21 1/2	@	32
Japan Wax.....	Lb.	12 1/2	@	13
Lard Oil (prime winter).....	Gal.	93	@	95
Linseed Oil (raw).....	Gal.	51	@	52
Menhaden Oil (crude).....	Gal.	nominal		
Neatsfoot Oil (20°).....	Gal.	96	@	98
Paraffine (crude, 120 & 122 m. p.).....	Lb.	3 1/2	@	3 1/4
Paraffine Oil (high viscosity).....	Gal.	27	@	28
Rosin ("F" grade) (280 lbs.).....	Bbl.	4.40	@	4.45
Rosin Oil (first run).....	Gal.	27	@	28
Shellac, T. N.....	Lb.	16	@	17
Spermaceti (cake).....	Lb.	30	@	35
Sperm Oil (bleached winter), 38°.....	Gal.	72	@	74
Spindle Oil, No. 200.....	Gal.	17	@	17 1/2
Stearic Acid (double-pressed).....	Lb.	9	@	12
Tallow (acidless).....	Gal.	65	@	66
Tar Oil (distilled).....	Gal.	30	@	31
Turpentine (spirits of).....	Gal.	49 1/2	@	50

## METALS

Aluminum (No. 1 ingots).....	Lb.	17 3/4	@	18 3/4
Antimony (Hallet's).....	Lb.	2	@	2 1/4
Bismuth (New York).....	Lb.	2.05	@	2.10
Bronze powder.....	Lb.	50	@	3.00
Copper (electrolytic).....	C.	14.30	@	14.50
Copper (lake).....	Lb.	14 1/2	@	14 1/4
Lead, N. Y.....	Lb.	4	@	—
Nickel.....	Lb.	50	@	55
Platinum (refined).....	Oz.	43.50	@	44.50
Silver.....	Oz.	88	@	—
Tin.....	C.	38.00	@	—
Zinc.....	C.	5.30	@	5.35

## FERTILIZER MATERIALS

Ammonium Sulfate.....	C.	2.85	@	2.90
Blood, dried.....	Unit	nominal		
Bone, 4 1/2 & 50, ground, raw.....	Ton	29.00	@	30.00
Calcium Nitrate (Norwegian).....	C.	2.05	@	2.15
Castor meal.....	Unit	nominal		
Fish Scrap, domestic, dried.....	Unit	nominal		
Phosphate, acid, 16 per cent bulk.....	Ton	7.00	@	—
Phosphate rock (f. o. b. mine).....	Ton	2.75	@	3.00
Florida land pebble, 68 per cent.....	Ton	5.00	@	5.50
Tennessee, 70-80 per cent.....	Ton	39.07	@	—
Potassium, "muriate," basis 80 per cent.....	Unit	0.13	@	—
Pyrites, furnace size, imported.....	Unit	3.50	@	—
Tankage, high grade.....	Unit	3.50	@	—

# The Journal of Industrial and Engineering Chemistry

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No. 5

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## TABLE OF CONTENTS

### EDITORIALS:

The Spring Meeting at Cincinnati.....	364
Journal of the American Water Works Association.....	365
The Distribution of Industries.....	365
New Section Added to Journal.....	366

### ORIGINAL PAPERS:

Study of the Composition of Water Gas Tar. By C. R. Downs and A. L. Dean.....	366
The Radioactivity of Some Type Soils of the United States. By Richard B. Moore.....	370
Partial and Intermittent Combustion of Gas. By E. E. Somermeier.....	374
Wood Distillation under Diminished Pressure—A Contribution to the Problem of Utilization of Wood Waste. By Maxwell Adams and Charles Hilton.....	378
The Nature of Basic Lead Carbonate. By Edwin Euston.....	382
Thermal Reactions in Carbureting Water Gas. Part I—Theoretical. By M. C. Whitaker and W. F. Rittman.....	383
Paraffin Bodies in Coal Tar Creosote and Their Bearing on Specifications. By S. R. Church and John Morris Weiss.....	396
A Volumetric Method for the Determination of Lead. By Alfred Alder and M. F. Coolbaugh.....	398
The Determination of Arsenic in Hydrochloric and Sulfuric Acids. By R. F. Tarbell.....	400
One Cause of Low Results in the Assay of Peppermint Oil. By Harry W. Redfield.....	401
Observations upon the Assay of Digestive Ferments. By Howard T. Graber.....	402
Laboratory Studies on Malt Extract. By Howard T. Graber.....	403

### LABORATORY AND PLANT:

The Pyrometer in the Assay Muffle. By Frederic P. Dewey.....	405
Approved Bureau of Mines Experiment Station at Pittsburgh.....	406
The Chemist's Duplex Slide Rule. By H. H. Hanson.....	407

### ADDRESSES:

The Chemists' Club. By William L. Dudley.....	407
Chemical Abstracting. By John J. Miller.....	411
The Present State of the Cyanamid Industry. By E. J. Pranke.....	415

Industrial Maltose. By Chester B. Duryea.....	419
Milling of Wheat and Testing of Flour. By Harry McCormack.....	423

### CURRENT INDUSTRIAL NEWS:

Fuller's Earth.....	428
Financial and Labor Conditions on English Railroads	428
Imports of Spermin Oil during 1913.....	429
Potash Shipments during 1914.....	429
By-Product Producers in Germany.....	429
German Foreign Trade in Iron.....	429
Natural Gas in Canada.....	430
Tar and Benzol Prices.....	430
Domestic Lighting Fifty Years Ago.....	430
Gases in Iron and Steel.....	430
The Cinematograph in Research.....	430
Chemical Industries in Japan since 1911.....	431
The Paper Industry in India.....	431

### SCIENTIFIC SOCIETIES:

American Chemical Society—Forty-Ninth Meeting, Cincinnati, April 6-10, 1914.....	431
Industrial Chemists and Chemical Engineers Division—Report of Committee on Alum Specifications.....	435
The American Electrochemical Society—Twenty-Fifth General Meeting, New York City, April 16-18, 1914	436
Presidential Address—Some Economic and Aesthetic Aspects of Electrochemistry. By E. F. Roerber.....	436
The American Institute of Electrical Engineers—293rd Meeting.....	439

### NOTES AND CORRESPONDENCE:

The Invention of Celluloid.....	440
Laboratories in the Chemists' Building.....	441
An Investigation of the Presence of Furfural in Cider Vinegar—A Correction.....	441
Correction.....	441

### PERSONAL NOTES.....

### GOVERNMENT PUBLICATIONS.....

### PERSONAL NOTES.....

### BOOK REVIEWS:

Molded Electrical Insulation and Plastics; Die Chemie und Technologie der Natürlichen und Künstlichen Asphalte; Solvent Oils, Gums, Waxes and Allied Substances; Practical Science for Engineering Students.....	446
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### NEW PUBLICATIONS.....

### MARKET REPORT.....



## EDITORIALS

### THE SPRING MEETING AT CINCINNATI

The Forty-ninth Meeting of the American Chemical Society convened in Cincinnati, April 6th-10th; the total registration was 658. The sessions were held at the University of Cincinnati, twenty minutes' ride from the headquarters at the Hotel Sinton.

The business meeting of the Council on Monday evening was devoted to committee reports. The report of the Supervisory Committee on Standard Methods of Analysis was discussed at length. A tentative report of the special Committee on Business Management was made by Prof. Baskerville. After some discussion it was accepted as a report of progress and the committee was requested to submit it, with a statement of the reasons for and against the plan proposed, to the Council and local sections before May 15th, in order that final action may be taken at the Annual Meeting at Montreal this fall.

The formal opening of the convention was the General Meeting in McMicken Hall, where the Society was welcomed by the Honorable F. S. Spiegel, Mayor of Cincinnati, and by President Charles W. Dabney of the University of Cincinnati. President T. W. Richards responded to their cordial greetings and congratulated the Society on the recently made statement that the twentieth century is to be a chemical century. The scientific program is printed in full in this issue.

The Local Executive Committee, consisting of F. W. Weissmann, Stephen J. Hauser and Archibald Campbell, deserve the unbounded gratitude of the Society for the manner in which they handled the many details of the meeting. Arrangements were made with the University of Cincinnati for serving luncheon each day at the University, and this was of special convenience to those taking part in the many excursions. These trips were in charge of Mr. G. Farnham and included the inspection of twenty-four important industrial plants and points of interest in the vicinity of Cincinnati, and visits to the National Cash Register Factory at Dayton, Ohio, and the American Rolling Mills at Middletown, Ohio. Special street cars or automobiles were furnished so that the minimum fatigue might result from the inspection of large plants. Special trains took the visitors to the Dayton and Middletown factories. Further details as to these instructive and enjoyable excursions will be found elsewhere in this Journal.

On Tuesday evening, the complimentary smoker was given at the Hotel Sinton. Ample supplies of food and favorite drinks were served along with choice brands of "smokes;" the members were provided with colored tissue paper caps which added to the gaiety of the occasion. Mr. E. B. Remelin humorously demonstrated the simplicity of several Modern Chemical Developments including the manufacture of synthetic rubber, the ease with which radium may be prepared in large quantities (according

to methods developed by Prof. Parsons) and its use in the rapid cure of malignant cancer. A cartoonist sketched favorite poses and well-known characteristics of prominent personalities in the Society, and the entertainment was concluded by a number of deft and pleasing sleight-of-hand tricks. Mr. Broeman and his committee received the thanks of all present for a most successful evening.

A notable entertainment was furnished by the Cincinnati Symphony Orchestra in a complimentary concert tendered to the visiting members of the Society by the Cincinnati Section at the Emery Auditorium on Wednesday evening with Dr. Ernst Kunwald conducting and Mr. Emil Heermann as violin soloist.

#### PROGRAM.

- |                                   |                 |
|-----------------------------------|-----------------|
| 1. Overture "Der Freischutz"..... | <i>Weber</i>    |
| 2. "Unfinished" Symphony.....     | <i>Schubert</i> |
| 3. Hungarian Rhapsody No. 1.....  | <i>Liszt</i>    |
| 4. Concerto Grosso No. 6.....     | <i>Haendel</i>  |
| Dr. Kunwald at the Piano.         |                 |
| 5. Violin Concerto.....           | <i>Bach</i>     |
| Emil Heermann.                    |                 |
| 6. Academische Fest Overture..... | <i>Brahms</i>   |

The program was rendered with a sympathy and delicacy of musical feeling that only careful training, finished technique and perfect ensemble work can make possible. The enjoyment of the audience was attested by hearty applause and appreciative compliments from the many music lovers in the Society.

Previous to the Symphony Concert the abstractors and editors of the Society's Journals were served an excellent dinner in the dining room of the Ohio Mechanics Institute. Various suggestions as to the improvement and more extended distribution of the Society Journals were informally discussed. About thirty guests were present and it is hoped that such meetings of our editorial force may become an integral part of our general meetings, since they will afford an excellent stimulus to the cooperation necessary for the best success of the Society's publications.

The Banquet on Thursday evening at the Hotel Sinton was attended by over two hundred guests. The large banquet hall was artistically decorated with pink carnations, ferns and smilax, and an exquisite musical program was rendered during the evening. Prof. Wilder D. Bancroft acted as Toastmaster and addresses were made by Charles W. Dabney, Theodore W. Richards, Albert Bettinger and John Uri Lloyd. The Society owes much to the Banquet Committee, headed by Mr. Lauder W. Jones, for bringing the Cincinnati part of the meeting to a close with such a delightful social function.

Ladies to the number of one hundred and twenty-five attended the meeting. Their comfort and enjoyment were provided for by a large committee under the efficient leadership of Mrs. J. W. Ellms. About seventy guests attended the complimentary dinner



DELEGATES OF THE FORTY-NINTH MEETING OF THE AMERICAN CHEMICAL SOCIETY AT THE NATIONAL CASH REGISTER PLANT, DAYTON

served to the ladies at the Hotel Sinton on Tuesday evening when interesting talks were made by some of the members and several of the guests who had been connected with pure food campaigns in the large cities. The dinner was followed by a very enjoyable theatre party to which the guests were conveyed in automobiles. Wednesday was spent at Ft. Thomas and Thursday at the Rookwood Pottery. All of the regular division meetings and excursions were open to the ladies. A large number took the Dayton-Middletown trip, the ride thence being shortened by piano and vocal solos as well as folk songs in which the entire party joined.

The industrial activity of the Queen City of the West, the use of its University for the meetings, the hospitality of the many institutions and factories so graciously thrown open, the general comfort brought about by the skillful planning of the committees of the Local Section, will linger long in the memories of those who attended the Spring Meeting at Cincinnati.

#### JOURNAL OF THE AMERICAN WATER WORKS ASSOCIATION

We have just received the first number, March, 1914, of the *Journal of the American Water Works Association*. This Journal is to take the place of the annual proceedings, and marks a great step in advance in the affairs of the Association, which is now thirty-four years old. At the last convention of the Association, a new constitution was adopted giving it an organization resembling, in several features, that of the American Chemical Society. The formation of sections was authorized, and already a New York Section has been formed that has had two successful meetings. The expansion under the new constitution requires a more prompt medium for the production of the proceedings and papers and therefore, the executive committee of the Association has established a quarterly journal.

It is planned to issue the first number each year before the annual convention. It will contain papers, which will later be discussed at the convention. A

second number will contain the proceedings of the convention and such papers and discussions as may be promptly available for publication. The third and fourth numbers will contain the remaining papers and discussions from the annual convention, publish additional papers submitted to the sections, make necessary announcements of local meetings and contain a revised list of members.

By this procedure the Association will present its papers more promptly, avoiding the delays attendant on a single annual issue. The Journal will furnish a repository for water works literature, which will bring it in closer touch with the needs and interests of the membership, besides offering a greater incentive to contributors.

The first number contains nine papers. From the character of these we see that the new journal will deal with matters of interest to a large variety of readers including chemists, bacteriologists, engineers, administrators, and practical water works operators.

We hope that this new departure will make the American Water Works Association a greater benefit than ever before to its members.

#### THE DISTRIBUTION OF INDUSTRIES

In a communication to the National Liberal Immigration League, Dr. C. W. Eliot presents his remedy for municipal congestion. In his opinion, the prevention of the overcrowding of our industrial centers and the evils attending this overcrowding lies not in restricting immigration, but in the distribution of industrial plants throughout the country.

This is a matter which has already received considerable attention by economists, though not as exhaustively as it might deserve, if the fundamental conditions did not require so radical a change to make it practicable. The main factor which attracts industries in American cities is the concentration of lines of transportation at those points. Were transportation rates always as low at rural points as at the cities, the task would be greatly simplified. Doctor Eliot is of the opinion that the project is now easier

because of the parcel post development, the growth of trolley lines, and freight and automobile trucks. However, industrial growth will depend on cheap railroad rates for fuel and raw materials and for shipment of finished products to a degree which will make the other means of transportation hardly worthy of consideration.

On the other hand, there are certain characteristics in rural locations which are attractive for industrial enterprises. The cost of sites for factories and residences of employees, the ability of workmen to have their own gardens, the facility for waste disposal, can, if the fundamental conditions be made right, work a practical revolution. But transportation conditions are the vital point and the scheme will be impracticable until the rural point can be guaranteed the same transportation rates as the city.

W. A. HAMOR

#### NEW SECTION ADDED TO JOURNAL

A new section on GOVERNMENT PUBLICATIONS has been added to the JOURNAL, beginning in this issue, under the editorship of R. S. McBride, Associate Chemist in the Bureau of Standards. This work is

planned to bring to chemists and engineers prompt notice of all government reports of interest to them, and to briefly and clearly review the scope and purpose of these publications. It is not intended that the articles shall be fully abstracted, since the work of *Chemical Abstracts* in this line should not be duplicated; but a prompt announcement of the publications will do a great deal to assist the chemical profession in taking advantage of the material now being issued by the Government. It will certainly be more convenient for the members of our Society thus to have condensed into one list the announcements previously scattered through a number of lists appearing at irregular intervals from the various departments. All Government Printing Office publications of value to chemists will be reviewed, including those which have appeared since January 1, 1914. The items of industrial importance appearing in the *Daily Consular Reports* will also be abstracted, beginning with March 1, 1914.

It is our belief that this up-to-date summary of the important investigations and publications of the Government will be of immense value to our profession.

## ORIGINAL PAPERS

### STUDY OF THE COMPOSITION OF WATER GAS TAR

By C. R. DOWNS AND A. L. DEAN

Received February 17, 1914

Water gas tar, more properly carburetted water gas tar, is the tarry product separating out in the purifying systems of plants manufacturing carburetted water gas. It is much less viscous than ordinary coal tar, with a distinctly different odor, due in part to the absence of the phenols and bases characteristic of coal tar. It is understood that a portion of the petroleum used in carburetting, after passing through various molecular changes, appears finally as tar, but of the exact nature of the transformations little is definitely known. It is, of course, the object of the gas maker to change as large a percentage of his gas oil into permanent gases as possible and keep the production of tar to the lowest limit.

A search through the literature for data concerning water gas tar yields but fragmentary and inadequate results. A. H. Elliott,<sup>1</sup> Matthews and Goulden,<sup>2</sup> and C. N. Forrest<sup>3</sup> have recorded the results of fractional distillations of the tar, and Dean and Bateman,<sup>4</sup> S. P. Sadler,<sup>5</sup> and Forrest<sup>3</sup> have furnished information regarding the composition of the creosote oils derived from water gas tar. Some of the statements to be found in the literature refer to material clearly quite different from the water gas tar produced in the standard American installations of the present day. Thus Matthews and Goulden's tar was lighter than water and contained 8.51 per cent of "light paraffins."

The data presented in this paper were obtained on water gas tar from the purifying system served by several standard Lowe system water gas sets. The carburetting oil in use at the time was derived from Oklahoma crudes. As might be predicted, the tar separating at different points along the purifying system, as the gas passes from the sets to the final stages of purification, becomes progressively lighter and richer in the more volatile constituents.<sup>1</sup> Mixed tar from the whole system was used for the work described in the present paper.

#### SYSTEMATIC FRACTIONAL DISTILLATIONS

A series of detailed fractional distillations was carried out with a view to locating the boiling points of any individual compounds which might be present in substantial amounts. The first distillation of the tar up to 250° C. was carried out in a five gallon

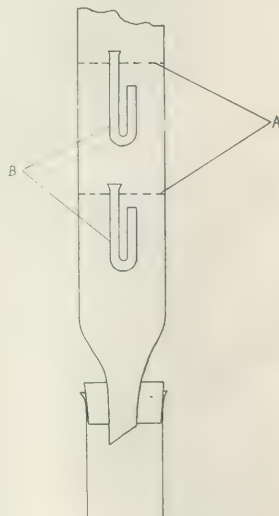


FIG. 1.—CHAMBERS OF DEPHLEGMATOR  
A, PERFORATED GLASS PLATES  
B, SIPHON TUBES

<sup>1</sup> Am. Chem. Jour., 6, 248.

<sup>2</sup> Gas World, 16, 625.

<sup>3</sup> Jour. Soc. Chem. Ind., 30, 193.

<sup>4</sup> U. S. Forest Service, Circular 112.

<sup>5</sup> Trans. Am. Inst. Chem. Eng., 2, 177.

<sup>1</sup> Dean and Downs, THIS JOURNAL, 3, 108.



copper still, the distillation being effected by immersing a resistance coil in the tar. The distillates thus obtained constituted the "First Series" of fractions, and the

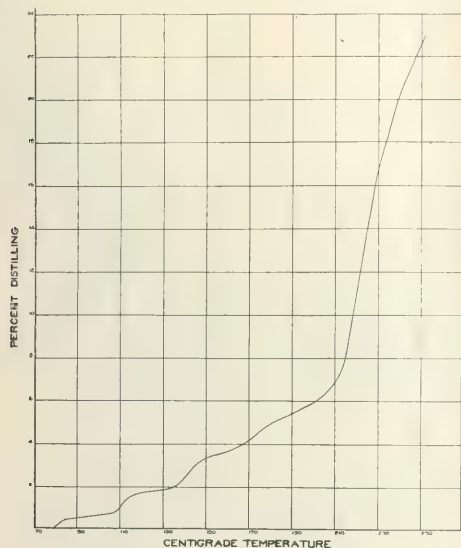


FIG. 2—THIRD SERIES DISTILLATION

residue was saved for later study. These first fractions were then refracted from an electrically heated glass flask provided with a Hempel column, yielding the "Second Series." In refracting the second and subsequent distillates a modified Young dephlegmator was employed up to 200° C., and above that the Hempel column. This Young dephlegmator consisted of six chambers, the floors of which consisted of perforated glass plates provided with overflow tubes as

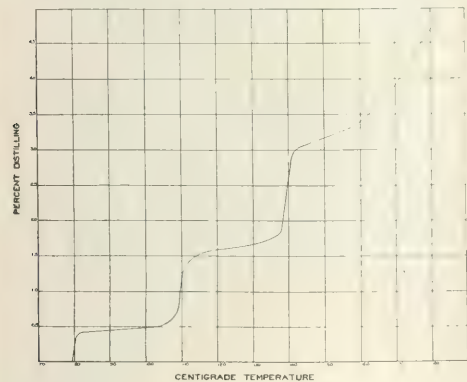


FIG. 3—SIXTH SERIES DISTILLATION

indicated in Fig. 1. To avoid excessive condensation in the chambers the dephlegmator was air-jacketed up to 110° C., and above that enclosed in an asbestos sheath heated by resistance wires. In this way the process of repeated fractionation, according to the

common practice of handling the fractions in such work, was continued to the "Third Series" of fractions boiling up to 250° C. and to the "Sixth Series" with the lower boiling portions. The curves of the third and sixth series are shown in Figs. 2 and 3.

From Fig. 2 it is clear that the largest single constituent boils at about 220° C., approximately the boiling point of naphthalene. The abrupt rises in Fig. 3 at 80°, 110° and 140° C. indicate the presence of appreciable amounts of individual substances boiling near these temperatures, which were subsequently proven to be benzene, toluene, and the xylenes. A smaller irregularity appears near the boiling point of mesitylene, 164.5° C. It is believed that a fairly satisfactory separation had been achieved in this sixth series, and during considerable portions of the distillation when the distillates appeared to be nearly pure compounds, fractions were taken at each degree rise in temperature and corrections made for the emergent thermometer stem.

#### GENERAL CHARACTERISTICS OF THE DISTILLATES

INDICES OF REFRACTION—The indices of refraction of the fractions of the fifth series were determined at 30° C. with the results shown in the following table:

Temp of fraction ° C.	Refractive index at 30° C.	Temp. of fraction ° C.	Refractive index at 30° C.
79-83	1.4938	125-130	1.4916
83-85	1.4938	130-137	1.4935
85-90	1.4933	137-145	1.4967
90-95	1.4923	145-150	1.4987
95-100	1.4921	150-155	1.4976
100-109	1.4910	155-160	1.4968
109-113	1.4909	160-165	1.4979
113-115	1.4910	165-172	1.5030
115-120	1.4908	172-179	1.5180
120-125	1.4912	179-185	1.5269

#### BROMINE ABSORPTION

The bromine absorptions of the fractions were used as a relative measure of the unsaturated hydrocarbons. The determinations were made by allowing an excess of a tenth normal solution of bromine in carbon tetra-

Sixth series fractions ° C.	G. Br added per cc.	Third series fractions ° C.	G. Br added per cc.
78.9-79.7	0.0133	180-205	0.4487
79.7-80.7	0.0181	205-235	0.2526
80.7-85.0	0.0133	235-250	0.1629
85.0-92.0	0.0182		
92-101	0.0192	Second series fractions	
101-109	0.0141	250-260	0.0479
109-110.5	0.0104	260-270	0.0432
110.5-114	0.0133	270-280	0.0610
114-120	0.0247	280-290	0.0442
120-130	0.0364	290-300	0.0963
130-138	0.0671	300-310	0.0771
138-142.5	0.1098	310-320	0.0700
142.5-145	0.1724		
145-150	0.2186		
150-155	0.1832		
155-160	0.1616		
160-164	0.1522		
164-167	0.4176		
167-172	0.4824		
172-177	0.4008		
177-182	0.5520		

chloride to react on 1 cc. of a sample for 15 minutes, the vessel containing the mixture being immersed in a bath of ice and salt and kept in the dark. After this

reaction period the unused bromine and the hydrobromic acid formed were both determined, and from these determinations the grams of bromine added per cubic centimeter of oil could readily be calculated.

#### "PARAFFINS"

Since the hydrocarbons of water gas tar have their origin in petroleum oil it might be supposed that considerable quantities of "paraffins" would be found in the distillate therefrom. To throw light on this point the fractions were sulfonated with concentrated sulfuric acid and the percentage by volume of the unsulfonated residues determined.

Temp of fraction 6th series	Per cent Unsulfonated	Temp of fraction 6th series	Per cent unsulfonated
75-79	0.06	138-142.5	1.2
79-90	None	142.5-145	2.4
80-81	None	145-150	1.2
81-85	None	150-155	2.2
85-92	None	155-161	1.6
92-101	None	161-166.5	1.8
101-109	None	166.5-172	1.6
109-110.5	None	172-177	None
110.5-114	None	3rd series	
114-120	None	180-205	55.0
120-130	0.4	205-235	1.4
130-138	0.4	235-250	2.2

The extraordinarily high percentage in the distillate from 180°-205° calls for some comment. The residues from all the other fractions were washed to clear oils, but the material obtained here was of putty-like consistency and resinous odor, and appeared to be a polymerization product of some unsaturated hydrocarbon rather than a "paraffin."

#### LOW-BOILING FRACTION

On repeated distillation of the first fractions below 75° C. a small amount of a very volatile liquid was obtained, boiling between 44° C. and 65° C., most of it coming over between 60° and 62°.

So small a quantity of this material was obtained that anything more than a few qualitative tests was not feasible. It charred and left no residue of undissolved oil when treated with concentrated sulfuric acid. It reacted violently with strong nitric acid, and absorbed bromine rapidly from bromine water, forming a brominated product heavier than water. No test for sulfur could be obtained. These tests combine to indicate a hydrocarbon mixture of markedly unsaturated character.

#### THIOPHEN

The sulfur containing compound thiophen ( $C_4H_4S$ ) appears to be always associated with benzol in coal tar light oil. Because of the closeness of its boiling point (84° C.) to that of benzol, it cannot be removed by fractional distillation. The presence of thiophen in water gas tar distillates was indicated by the indophenine test with isatin and concentrated sulfuric acid. The method of Deniges<sup>1</sup> was followed in making quantitative estimations of this compound. The average of thirteen analyses of the fractions between 79° C. and 90° C. was 2.1 per cent.

Tests for the higher homologues of thiophen were obtained with the higher boiling fractions, but no quantitative estimations were attempted.

#### BENZENE

An inspection of the distillation curve of the sixth series shows a decided rise at the boiling point of benzene, indicating the presence of about 0.4 per cent of that compound. The distillate between 79° and 81° could be readily nitrated, giving a good yield of nitrobenzol boiling between 106.5° and 107.5° and showing no evidence of "paraffins" by the method given by Lunge.<sup>1</sup> Dinitrobenzene, melting point 90°, and aniline distilling between 182° and 185° were also prepared from the purified benzene obtained from water gas tar. The aniline was colorless and turned only slightly brown on standing four months protected from sunlight.

A number of samples were prepared conforming to the requirements of the commercial grades of benzol. The starting material was a crude light oil obtained in the initial distillation of water gas tar in a large still. This was fractionated up to 180° C. from a large plain distilling bulb and the distillate refractioned through a Hempel column taking the following fractions:

1.....	68°-79°
2.....	79°-100°
3.....	100°-125°
4.....	125°-155°

Pure benzene was prepared from the fraction No. 2 by agitating with concentrated sulfuric acid, followed by washing with dilute acid and water, and agitation with caustic soda solution followed by thorough washing. Under laboratory conditions a loss of 4 per cent was experienced by these treatments. The washed product was carefully redistilled with a Hempel column and Young dephlegmator, yielding a product of correct boiling point. This c. p. benzene gave no test for thiophen, no discoloration with concentrated sulfuric acid, was of sweet odor and has shown no yellowing on standing for two years.

Preparations of 90 per cent benzol and 50 per cent benzol were also made from water gas tar light oil by fractional distillation and washing with sulfuric acid and caustic soda. With these products much less exact fractional distillation was required than with the c. p. benzol. Both preparations were free from thiophen, gave no color with concentrated sulfuric acid, and have remained water white and sweet for two years. The loss in washing was small.

In preparing 160° benzol or solvent naphtha the same general process of washing was followed but the loss in washing was much greater, amounting to over 15 per cent. The product was of good color and odor, and gave but a very pale straw color with concentrated sulfuric acid.

#### TOLUENE

An inspection of the "Sixth Series" distillation curve shows a rise of about 0.8 per cent at the boiling point of toluene. A portion of this fraction of the sixth series was nitrated, giving 85 per cent of the theoretical yield, and showing but a trace of paraffins.

The fraction No. 3 from the Hempel column distillation mentioned under "Benzene" above was washed with sulfuric acid and alkali (with a loss of 6 per cent)

<sup>1</sup> *Compt. rend.*, 90, 781.

<sup>1</sup> *Coal Tar and Ammonia*, 3rd Edition, p. 641

and the washed oil fractionated with a Hempel column. The fraction  $95^{\circ}$ – $120^{\circ}$  was redistilled with the same apparatus and the fraction  $109.5^{\circ}$ – $111.5^{\circ}$  taken. This product compared favorably with standard makes of C. P. toluene and gave no test for thiobutylene and no color with concentrated sulfuric acid.

#### XYLENES

The next decided rise in the distillation curve after that at the toluene fraction appears around  $140^{\circ}$ , suggesting the presence of xylenes. The curve indicated about 1.2 per cent of these hydrocarbons.

The separation of the three isomeric xylenes by fractional distillation is not feasible because of the nearness of their boiling points. By the use of Levenstein's method<sup>1</sup> one sample of xylene fraction yielded 75 per cent metaxylene, 20 per cent para, and, by difference, 5 per cent of the ortho. On another sample of water gas tar the results were 77 per cent meta, 19.5 per cent para, 2.0 per cent ortho, and 1.5 per cent "paraffins." It is doubtful whether the ortho-xylene is present in more than traces since a qualitative test<sup>2</sup> failed to reveal its presence.

The sodium salts of the ortho- and meta-xylene sulfuric acids were prepared according to Jacobsen.<sup>3</sup> The needle-like crystals similar to those described for the ortho salt were only present in very small amounts. Metaxylene boiling  $138^{\circ}$ – $139^{\circ}$  was prepared according to Jacobsen by decomposing the meta-xylene sulfuric acid.

#### MESITYLENE

A slight irregularity of the distillation curve around  $165^{\circ}$  suggested the presence of mesitylene. The "Sixth Series" distillate obtained at this point was twice redistilled with a Glinsky dephlegmator and the distillate between  $164^{\circ}$  and  $167^{\circ}$  nitrated. A solid nitro-compound was obtained which after careful washing and recrystallization gave a constant melting point of  $236^{\circ}$ . The nitration of another portion gave a product melting at  $235^{\circ}$ . Mulliken gives the melting point of trinitro mesitylene as  $235^{\circ}$  C.

From the alcohol used to wash the crystals of trinitro mesitylene a small crop of barrel-shaped crystals was obtained which on repeated recrystallization gave a melting point of  $167^{\circ}$ , and contained 16.31 per cent of nitrogen. The theoretical nitrogen content of trinitro-trimethyl benzenes is 16.47 per cent, but the melting point is far too low for trinitro pseudocumene. The amount of this compound was too small for further experiments, and it remained unidentified.

#### NAPHTHALENE

Inspection of the distillation curve for the third series shows that the most decided rise in the whole curve appears between  $215^{\circ}$  and  $235^{\circ}$ , indicating a relatively large proportion of naphthalene. An attempt was made to estimate the amount of naphthalene in water gas tar as follows: 500 grams of tar were distilled to  $260^{\circ}$  C. and the naphthalene separating in the distillate

filtered off and pressed in a screw press; the filtrate was placed in a freezing mixture and the new crop of naphthalene crystals similarly removed; this filtrate was distilled collecting a fraction from  $185^{\circ}$ – $265^{\circ}$ , which was cooled, filtered and the naphthalene pressed; the new filtrate was refractionated, taking a fraction  $195^{\circ}$ – $235^{\circ}$ , which was similarly deprived of its naphthalene and the new filtrate distilled, collecting a fraction  $210^{\circ}$ – $225^{\circ}$ , which yielded but a very small separation of naphthalene when placed in a freezing mixture; the total weight of the solids thus recovered amounted to 8.0 per cent of the tar.

Naphthalene was prepared from the solids pressed from the distillate obtained from water gas tar between  $200^{\circ}$  and  $250^{\circ}$ . These solids were distilled, rejecting the first and last 10 per cent, and the distillate treated with sulfuric acid containing a little dichromate. The product, after thorough washing with water, was pressed and distilled, giving a product boiling at  $217^{\circ}$  C. (uncorrected) and melting at  $80^{\circ}$ , which showed no discoloration with concentrated sulfuric acid and remained perfectly white after an exposure of four months to the light.

#### ANTHRACENE

The above described experimental work was carried out for the most part on that part of the water gas tar which distilled below  $250^{\circ}$  C. in the initial distillation. The residue above  $250^{\circ}$  C. was worked up in collaboration with Dr. F. L. Haigh of this laboratory.

Two methods of distilling this residue were tried; in one the distillation was carried out with heat alone, in the other steam was introduced into the still in considerable volume. In both types of distillation most of the fractions showed a separation of solid materials on cooling. These solids were removed, pressed and weighed and the anthracene in them determined according to the method proposed by Meister, Lucius and Bruning,<sup>4</sup> "with appendix." This method consists in converting the anthracene into anthraquinone by treatment with chromic acid in glacial acetic acid solution. The anthraquinone was further purified by solution in fuming sulfuric acid and recovery therefrom by dilution.

The results of the dry distillation were as follows:

Temperature ° C.	Per cent of solids in fractions	Per cent anthracene in solids	Tempera- ture ° C.	Per cent of solids in fractions	Per cent anthracene in solids
-265	None		335-345	4.19	41.75
265-305	None		345-355	4.27	34.85
305-315	1.32	65.49	355-360	3.39	26.41
315-325	2.32	61.35	360-370	4.36	7.41
325-335	3.85	42.82	370-400	None	

These results show the presence of 0.392 per cent of anthracene in the residue above  $250^{\circ}$ , equivalent to 0.29 per cent of the original tar.

The thermometer readings in the steam distillation were of little value; the fractions were accordingly cut at about each 250 cc. of oil distillate in distillations

<sup>1</sup> Jour. Soc. Chem. Ind., 4, 78

<sup>2</sup> Mulliken, "Identification of Pure Organic Compounds," Vol. I, p. 202.

<sup>3</sup> Ber., 10, 1009.

<sup>4</sup> Allen, "Commercial Organic Analysis," 3rd Ed., Vol. II, Pt. II, p. 229.



of 5000 grams of the "Residue." The solids were determined and analyzed with the results given below:

Fraction	Volume Cc.	Wt. of solids in fractions	Per cent of anthracene in solids
1.....	250	None	...
2.....	260	None	...
3.....	250	None	...
4.....	260	1.2	58.20
5.....	250	5.8	47.26
6.....	260	11.0	46.83
7.....	250	15.2	40.52
8.....	250	14.4	43.76
9.....	250	12.1	39.19
10.....	250	5.4	21.73
11.....	260	None	...
12.....	250	None	...

In the steam distillation, therefore, 0.517 per cent of anthracene was recovered from the "Residue" above 250°, equivalent to 0.383 per cent of the original tar. There was clearly less decomposition when steam was used, since the pitch contained but 5.6 per cent of free carbon, whereas that from the dry distillation averaged 57 per cent. Practically all of the anthracene comes over under 360° in the dry distillation, and at that temperature little cracking has taken place, the pitch containing but 6.0 per cent free carbon. Above 360° an orange-colored, viscous, semi-solid material appears in the distillate and seems to be indicative of marked decomposition.

Fairly pure anthracene was prepared from the expressed solids by washing with gasoline, and subliming the residue. This anthracene melted at 207°–211° C. and when mixed with a sample of Kahlebaum's anthracene, the mixture melted at 208°–211°.

As a further test of the quality of the solids pressed from the high boiling distillates of water gas tar, 50 grams of these solids recovered from the distillate between 289° and 361° were oxidized with bichromate and sulfuric acid. The anthraquinone after purification was sublimed giving 18.2 grams of crystalline anthraquinone. Anthraquinone prepared in this way was converted into the sodium anthraquinone-monosulfonate which in turn was converted into alizarine. A beautiful orange-red crystalline preparation of alizarine was obtained on subliming the product. Under laboratory conditions the transformation of anthraquinone into alizarine is difficult, and the yields obtained correspondingly low. From about 20 grams of anthraquinone only about 7 grams of alizarine were obtained.

#### SUMMARY

A systematic fractional distillation of water gas tar shows that it possesses a general resemblance to coal tar in its hydrocarbon content although, of course, the bases, phenols, and free carbon of the latter are absent or nearly so. The small amounts of material in the distillates resisting the action of sulfuric acid indicate an absence of paraffin and naphthene hydrocarbons, and the marked variation in the capacity for halogen addition points to variable amounts of unsaturated linkings outside the benzene ring.

Benzene, toluene, the xylenes, mesitylene, naphthalene, and anthracene were shown to be present in sub-

stantial amounts. The preparation of the pure hydrocarbons and of commercial products could be effected by methods similar to those employed with coal tar, and without encountering special difficulties.

It would appear probable that water gas tar may offer a commercial source of supply for the various grades of benzol and solvent naphtha. Naphthalene could readily be produced, but there is no adequate demand, and it is likely that the present trade conditions would not warrant the production of anthracene.

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#### THE RADIOACTIVITY OF SOME TYPE SOILS OF THE UNITED STATES

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Strutt<sup>1</sup> first called attention to the radioactivity of igneous and sedimentary rocks. The average of his results on igneous rocks showed a radium content of  $3.3 \times 10^{-12}$  grams of radium per gram of rock. The radium content of the sedimentaries was somewhat less. Joly<sup>2</sup> has examined a large number of rocks for radium and thorium. His radium values are somewhat larger than those of Strutt and other workers. The average of a number of his thorium determinations indicates the presence of  $1.58 \times 10^{-8}$  grams of thorium per gram of rock. Fletcher,<sup>3</sup> working primarily with secondary rocks, has confirmed Joly's results and at the same time pointed out that, with the exception of the calcareous rocks, those of the same types have always very nearly the same radium content.

Although a considerable amount of work has been done on the radioactivity of rocks and minerals, very little has been attempted along this line with soils. A knowledge that the atmosphere was radioactive was naturally followed by an investigation of the activity of the underground air. Elster and Geitel, Bumstead, Blanc, Gadourian, Wilson, Ebert, Eve, Sanders, Satterly and others have contributed to our knowledge of this subject. Whereas a study of the underground air indicates very plainly that the soil is radioactive, it does not give any absolute values for the activity of the soil itself, as the activity of the underground air depends as much upon the emanating power of the radioactive matter in the soil as it does upon the amount of that material actually present. Some rough minimum determinations have been attempted. Wilson states that there is probably seven times as much thorium as uranium in the surface soils at Manchester. Blanc, on the other hand, estimates that from 5 per cent to 70 per cent of the activity of the Roman soil is due to thorium; while Sanderson's<sup>4</sup> work indicates that 1 cc. of soil at New Haven produces radium emanation in equilibrium with  $8.9 \times 10^{-14}$  grams of radium, and thorium emanation in equilibrium with  $1.35 \times 10^{-8}$  grams of thorium. Fletcher<sup>5</sup> gives the radium content

<sup>1</sup> *Proc. Roy. Soc.*, (A) **77** (1906), 472.

<sup>2</sup> *Phil. Mag.*, **17** (1909), 760; **18** (1909), 140; **23** (1912), 201.

<sup>3</sup> *Ibid.*, **23** (1912), 279.

<sup>4</sup> *Am. Jour. Sci.*, **32** (1911), 169.

<sup>5</sup> *Phil. Mag.*, **23** (1912), 279.

of two Dublin soils passing a 50-mesh sieve as  $5.2 \times 10^{-12}$  grams and  $2.8 \times 10^{-12}$  grams per gram of soil.

Strutt<sup>1</sup> states that the radium content of the Cambridge Gault is  $1 \times 10^{-12}$  grams per gram of material.

Satterly<sup>2</sup> measured the amount of radium emanation in the air of different soils at different intervals extending over a year. For depths of from 100-150 cm. in gravelly soil the amount of emanation is on the average  $200 \times 10^{-12}$  curies per liter. This is about 2,000 times as much as is usually in the atmosphere. He found that a liter of soil air was in association with 1200 grams of dry or 1400 grams of damp soil, and calculated from this that the apparent radium content of the soil is  $1.7 \times 10^{-14}$  grams per gram of dry soil. As the actual radium content of the soil is certainly very much larger than this, it follows that only a small portion of the emanation generated in the soil escapes under normal conditions from the soil particles into the air surrounding them.

Satterly also measured the proportion of radium emanation to thorium emanation in soil air at various depths. He found that the ratio increased from 1600 near the surface to 26,000 at a depth of 400 cm. At 150 cm. it is 8,600 and taking the radium content of the soil at  $1.1 \times 10^{-12}$  grams per gram of soil, he calculated that the thorium content would be  $1.4 \times 10^{-5}$  grams per gram of soil.

Apparently no systematic attempt has yet been made to correlate the radioactivity of soils with their other properties. Recently an elaborate study of the chemical composition of a number of type soils of the United States has been undertaken by G. H. Failyer and W. O. Robinson, of the U. S. Bureau of Soils. A mineralogical examination has been made of the same soils by Professor W. J. McCaughey. The author has these unpublished results at his disposal and has examined the soils for their radium content. The present paper constitutes a report on the results obtained.

Since radium is found in varying amounts in all rocks, spring waters, and even in underground waters, it is not surprising that botanists have tried the effects of the radium rays on the germination of seeds and the growth of plants. Since radioactivity is a factor of plant environment, it is possibly an agent in plant growth. Not only must the direct effect of the rays themselves be considered, but the chemical action induced by these rays, slight rises of temperature, etc., must be taken into account. The emanation, or gas, given off by radium salts diffuses through the soil, is dissolved by the soil solution, and comes in intimate contact with the plant roots even though the radium itself is in the soil as an insoluble sulfate or silicate. It is therefore more probable that if the presence of radium in the soil does affect the growth of plants appreciably, this effect will be more directly due to the influence of the emanation than to the radium. Some experimenters have not taken this fact into account and the influence of the  $\beta$  and  $\gamma$  rays on plants has in many cases been tested rather than bringing the roots in contact with the diluted emanation.

A far more serious objection to the experimental work with plants is that much greater amounts of radium have been employed than are ever present in the soil naturally, or likely to be added in actual agricultural or greenhouse practice. The amount normally present in soils is sensibly the same, namely, about 3 milligrams per acre foot. To increase this content one milligram per acre foot in the form of ground ore would cost about 20 dollars, and as pure radium salt about 120 dollars. The experimental work so far done indicates that at least several milligrams per acre would have to be added to produce an appreciable effect on the crop. Nevertheless, it seems well to call specific attention to some of the more important investigations in this direction.

Danyasz<sup>1</sup> found that the rays from radium and the emanation hindered all species of bacteria in their development, some varieties being more sensitive than others.

Dixon<sup>2</sup> stated that the growth of cress seedlings was retarded by the  $\beta$  and  $\gamma$  rays from radium salts. Dixon and Wigham also found that  $\beta$  rays exercised an inhibitory action on the growth of certain bacilli.

Germination of the spores of *Aspergillus niger*<sup>3</sup> was found by Koernicke to be inhibited by exposure to the  $\beta$  and  $\gamma$  rays. Generally speaking, he found that roots were more sensitive than shoots.

Hussakof,<sup>4</sup> in a review published in 1907, showed that up to the time of his publication there was a general agreement on the following conclusions:

- (1) The rays from radium affect the life processes of plants as well as animals. The Roentgen rays have a similar effect.
- (2) Different species of plants are affected differently in degree.
- (3) Younger tissues are more sensitive than older ones.
- (4) The general effect is to retard all activity. There are a few exceptions.
- (5) The growth and activity of enzymes are affected by the rays from radium.

Gager<sup>5</sup> found that in general the germination of both dry and wet seeds was retarded by the radium rays. Timothy grass seeds exposed to radium of weak activity showed an initial slowing up and then after five days an increased metabolism over the control culture. A similar result was obtained with bean seeds.

On the other hand, when unsoaked oat grains were planted at distances of 7, 22, and 45 mm. from a sealed glass tube containing 10 mg. radium bromide of 1,500,000 activity inserted in the soil, germination and subsequent growth were accelerated. The seeds farthest from the radium were accelerated most; those nearest, least. When timothy grass was grown in an atmosphere containing radium emanation, the result was dependent upon the amount of emanation used, the height above the soil at which the emanation was delivered, etc. Gager sums up by stating that "the

<sup>1</sup> *Compt. Rend. Acad. Sci. Paris*, **136** (1903), 461.

<sup>2</sup> *Nature*, **69** (1903), 5.

<sup>3</sup> *For. and Ind. Chem.*, **22** (1904), 155.

<sup>4</sup> *Med. Record*, **72**, July 20, 1907.

<sup>5</sup> *Memoirs New York Botanical Gardens*, **4** (1908).

<sup>1</sup> *Proc. Roy. Soc.*, (A) **78** (1906) 97.

<sup>2</sup> *Proc. Camb. Phil. Soc.*, **16**, p. 6.

rays of radium act as a stimulus to protoplasm. Retardation of growth following an exposure to the rays is an expression of overstimulation. Acceleration of growth indicates stimulation between a minimum and an optimum point."

Fabre<sup>1</sup> also studied the effect of radium emanation in the air on the germination of seeds and the growth of plants. The spores of *Sterigmatocystis nigra* on gelatin showed a retarded growth when exposed to strong doses of the emanation, the retardation being very largely proportionate to the amount of emanation. With *Linum catharticum* the germination of the seeds and the development of the plants were increased by increasing doses up to 1.5 microcuries per two liters of air. Above this, growth was retarded. It required a larger amount of emanation to retard germination. There seemed to be, however, an appreciable increase in the number of leaves developed on plants subjected to radium rays.

Acqua<sup>2</sup> gives the results of the effect of radium rays on the germination of seeds, development of seedlings, growth of pollen tubes and movements of protoplasm in several green plants. Great differences in reaction to the rays existed between different species and even between different organs of the same species. The root system generally responded when a more or less complete arrest of development was shown, although there were many exceptions. The aerial parts proved highly resistant, showing no general response either in stems or foliage. The pollen gave diverse results, some not growing at all, while others gave no reaction to the rays. Protoplasmic movements seem to be totally unaffected.

#### RADIUM CONTENT OF THE SOILS

All samples of soil used in this investigation were obtained by putting through a sieve of six meshes to the linear inch and grinding to an impalpable powder. Strutt's<sup>3</sup> method of getting the material in solution was used. The soil was fused with four times its weight of mixed alkali carbonates, treated with water, filtered, the residue washed with sodium carbonate solution to prevent hydrolysis, and then dissolved in hydrochloric acid. After standing a month, the combined emanation from the alkaline and acid solutions was introduced into the electroscope, which was of the C. T. R. Wilson type, modified by Boltwood.<sup>4</sup>

The standard used is that suggested by Boltwood.<sup>5</sup> It depends upon the fact that in old uranium minerals, the radium present bears a constant ratio to the uranium content of the mineral. Expressed in figures, 1 gram of uranium is in radioactive equilibrium with  $3.3 \times 10^{-7}$  grams of radium. Therefore, if the percentage of uranium in such a mineral is known, the amount of radium present is also known, and the emanation obtained from this radium can be used for standardizing the electroscope providing a correction is made for the amount of emanation which naturally

escapes at ordinary temperatures from the particular sample of mineral used. This must be determined for every sample of uranium mineral used for standardization.

McCoy<sup>1</sup> and Boltwood<sup>2</sup> showed that the ratio of radium to uranium in primary minerals, such as pitchblende, was constant. Their results were confirmed by Marckwald and Russell.<sup>3</sup> Mlle. Gleditsch,<sup>4</sup> however, obtained different ratios for different samples of pitchblende and following this there was a tendency to use dilute solutions of a pure radium salt as a standard. From such solutions, however, a portion of the radium nearly always precipitates sooner or later even though barium chloride is added. Heimann and Marckwald<sup>5</sup> have recently taken the matter up again and obtained the same ratio of radium to uranium in eight samples of pitchblende from different parts of the world, the average error being less than 0.5 per cent. It seems to be preferable, therefore, to use an analyzed pitchblende as a standard rather than a solution containing a radium salt.

The apparatus used for boiling off the emanation from the pitchblende for standardizing, and from the solutions obtained from the soils, was that designed by Schlundt and Moore.<sup>6</sup> All of the well known designs of apparatus for this purpose have been tested and compared by Randall,<sup>7</sup> who finds that the two forms of apparatus used by Schlundt and Moore give the highest ionization currents and the more uniform results.

Joly<sup>8</sup> has criticized the radioactive results obtained by the present method of getting rocks and minerals in solution. He claims that it is almost impossible to get solutions perfectly limpid and the precipitated silica carries down with it some of the radium. Although this is true to some extent, fairly concordant results can be obtained in the case of rocks and minerals by its use. Much more difficulty is experienced with soils than with rocks. Hydrolysis nearly always takes place and the filtering process is both long and tedious. On standing a short time silica invariably separated from the solutions. This was filtered off and fused again with alkali carbonates, and the process repeated until clear solutions were obtained. Even with the greatest care, some of the solutions became turbid before the emanation was boiled off. In order to lessen the difficulty with the silica, some of the soils were first treated with hydrofluoric and a little sulfuric acid. After evaporation and ignition, they were fused with fusion mixture in the ordinary way. The addition of the sulfuric acid at first sight would seem to be inadvisable, but as the solutions obtained by this method remained more limpid, and as practically all soils contain both sulfates and barium, it was thought that the advantages would outweigh the disadvantages. The

<sup>1</sup> Ber. der deut. chem. Gesell., **36** (1903), 3093; Jour. Am. Chem. Soc., **27** (1905), 391.

<sup>2</sup> Phil. Mag., **9** (1905), 599.

<sup>3</sup> Ber. der deut. chem. Gesell., **44** (1911), 771.

<sup>4</sup> Le Radium, **8** (1911), 256.

<sup>5</sup> Jahrb. Rad. u. Elektron., **10** (1913), 299; Phys. Zeit., **14** (1913), 303.

<sup>6</sup> Jour. Phys. Chem., **9** (1905), 320.

<sup>7</sup> Trans. Am. Electrochem. Soc., **21** (1912).

<sup>8</sup> Phil. Mag., **22** (1911), 134.

<sup>1</sup> Compt. Rend. Soc. Biol., **70**, 187; **69**, 523; **70**, 419.

<sup>2</sup> Ann. Bot. Rome, [2] **8** (1910), 223, 238.

<sup>3</sup> Proc. Roy. Soc., (A) **77** (1906), 472.

<sup>4</sup> Am. Jour. Sci., 4th Ser., **18** (1904), 97.

<sup>5</sup> Ibid., **18** (1904), 381.



results obtained, however, seemed to be low, so duplicate samples of the soils treated in this manner were fused in the ordinary way and a comparison of the results is given in Table I. In column B the results are given when the soil was treated with hydrofluoric and sulfuric acids previous to fusion. Column A gives the results when these acids were not used.

TABLE I

NO	DEPTH	RADIUM (Gram $\times 10^{-12}$ per gram of soil)	
		A	B
1	Volusia silt loam, Naples, N. Y.	0 <sup>0</sup> -8" 0.93	3.76
2	Volusia silt loam, Naples, N. Y.	8"-36" 1.10	
3	Cecil clay, Charlotte, N. C.	0 <sup>0</sup> -6" 1.94	0.54
4	Cecil clay, Charlotte, N. C.	6"-36" 0.78	
5	Cecil sandy loam, Charlotte, N. C.	0 <sup>0</sup> -8" 1.26	0.28
6	Cecil sandy loam, Charlotte, N. C.	8"-36" 1.95	1.33
7	Durham sandy loam, Ancher, N. C.	0 <sup>0</sup> -10" 1.73	0.45
8	Durham sandy loam, Ancher, N. C.	10"-36" 1.66	
9	Norfolk sandy loam, Laurinburg, N. C.	0 <sup>0</sup> -14" 2.56	
10	Norfolk sandy loam, Laurinburg, N. C.	14"-36" 2.80	
11	Decatur clay loam, Hollywood, Ala.	0 <sup>0</sup> -4" 2.78	
12	Decatur clay loam, Hollywood, Ala.	4"-36" 1.52	1.27
13	Hagerstown loam, Hollywood, Ala.	0 <sup>0</sup> -8" 2.57	1.21
14	Hagerstown loam, Hollywood, Ala.	8"-36" 0.83	1.13

When the activity was determined both with the use of sulfuric and hydrofluoric acids, and without, the results in six of the eight cases were uniformly lower when sulfuric acid was used. In the case of the Volusia silt loam soil, which is an exception, the results are so much at variance with the others that a suspicion as to the reliability of the figure  $3.76 \times 10^{-12}$  at once arose. An examination of the records showed the possibility, though not the certainty, of a contamination of this solution owing to an accident. This possibility of contamination, however, should cause the above figure to be rejected. In the case of the Hagerstown loam the two values are close, but there is no explanation for the discrepancy with the other results. A preliminary report on this work<sup>1</sup> was made before the two methods were used on the same samples. This preliminary report, therefore, does not show the variations in the results obtained.

In four cases, as shown in Table II, the soil is more active than the subsoil; in three, the reverse is true. The average activity of the soils is  $1.97 \times 10^{-12}$ , and that of the subsoils is  $1.52 \times 10^{-12}$ .

There seems to be a fairly definite relationship between the activity and the combined amounts of barium and strontium. In the majority of cases the soil or subsoil which has the highest activity also has the largest amount of barium plus strontium. The Hagerstown loam and Decatur clay loam are exceptions, the soil of the latter having a considerably larger activity than the subsoil, but carries a little less barium and strontium. The same reaction holds fairly well with the amount of sulfur present. In the Cecil clay and Durham sandy loam the amount of sulfur in the soil and subsoil in each case is the same, although the activity of the soil is greater. In only one case, however, the Decatur clay loam again, are the figures actually reversed.

This relationship between the activity of the soil

and the amount of barium, strontium and sulfur present is not surprising. Since radium has an insoluble sulfate, which precipitates with the sulfates of barium and strontium, the above results seem to indicate that radium in the soil is very largely, if not entirely, in the form of sulfate.

The number of samples tested does not justify any attempt to correlate the activities of the different soils with their productivity. Such figures would be reliable only when a much larger number of results are available.

The amount of rare earths present in the soils as determined by Failyer and Robinson<sup>1</sup> was so small that no conclusion can be drawn by a comparison of the rare earth content with the amount of activity.

TABLE II

	ACTIVITY Gram $\times 10^{-12}$ per gram of material		BaO(a) and SrO(a)		SULFUR(a)	
	Soil	Subsoil	Soil	Subsoil	Soil	Subsoil
Cecil clay	1.94	0.78	0.10	0.05	0.07	0.07
Durham sandy loam	1.73	1.66	0.16	0.14	0.06	0.06
Decatur clay loam	2.78	1.52	0.06	0.07	0.13	0.19
Hagerstown loam	2.57	0.83	0.17	0.17	0.39	0.14
Volusia silt loam	0.93	1.10	0.08	0.10	0.09	0.10
Cecil sandy loam	1.26	1.95	0.05	0.05	0.04	0.09
Norfolk sandy loam	2.56	2.80	0.02	0.03	0.07	0.13
	13.77	10.64	0.64	0.61	0.85	0.78
Average	1.97	1.52	0.09	0.09	0.12	0.11

(a) Unpublished determinations by Failyer and Robinson.

Since the activity of at least secondary rocks of the same type is fairly constant, it would seem that there ought to be more connection between the mineralogical composition of a soil and its activity. Unfortunately, the mineralogical data at my disposal are not sufficiently complete to draw any such connection. Only the potash feldspars and micas were determined quantitatively—the others qualitatively, and as most rock-forming minerals occur in all soils, the qualitative results showed no significance. Monazite occurs in some soils, but was not specially looked for in the twelve samples examined and was not listed among the minerals in any of them.

#### THORIUM CONTENT OF THE SOILS

After experimenting with other methods,<sup>2</sup> that used by Joly for determining the thorium of rocks and minerals was finally decided on. Fig. 1 shows the apparatus. *A* is the flask containing the solution of the material to be tested. In this case it contained either the acid or alkaline solution obtained from fusion of the soil with fusion mixture. *B* is a drying tube containing at one end calcium chloride and at the other, phosphorus pentoxide, the two separated by a plug of glass wool. *C* is a tube of small diameter, with a bulb at the top and dipping at the bottom into a fairly heavy oil. *D* is the electroscope and at *E* there is a needle valve (not shown).

The flask *A* is first disconnected from the apparatus and the solution boiled vigorously for ten minutes. This is to get rid of the radium emanation. Thorium emanation is boiled off, of course, at the same time,

<sup>1</sup> Private communication.

<sup>2</sup> I desire to thank Mr. W. O. Robinson of the Bureau of Soils for valuable assistance in this part of the work.

<sup>1</sup> Orig. Com. 8th Intern. Congr. Appl. Chem.

but as the half-life period of the radium emanation is 4.8 days and that of the thorium emanation 54 seconds, the latter is very rapidly and the former very slowly reformed. Hence any active gas which is found in the solution after the ten minutes' boiling and during the progress of the experiment can be considered as thorium and not radium emanation.

The flask *A* is now connected with *B* and gently boiled while a constant current of air is drawn through the whole apparatus in the direction of the electroscopes. This current can be controlled by the needle valve. *C* assists in regulating the pressure in the apparatus. If the boiling is steady the leaf does not vibrate and readings are readily made.

If the air is pulled too rapidly through the apparatus, the emanation is too much diluted; if too slowly, a considerable portion of the emanation decays before it reaches the electroscopes. A maximum effect can therefore only be obtained by trial.

The activity of any given soil is, of course, the sum of the activities of the acid and alkaline solutions obtained from that soil.

The natural leak of the electroscopes under the experimental conditions is obtained by substituting for *A*, a similar flask containing distilled water and boiling as already described. It was noted that if air was

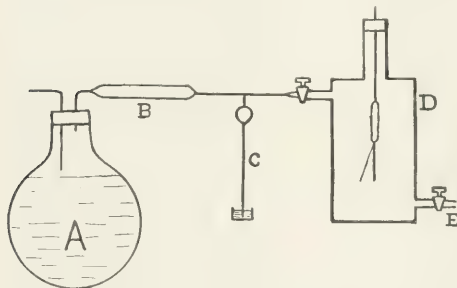


FIG. 1

passed over calcium chloride and phosphorus pentoxide and then through the electroscopes, the leak was smaller than when no air was passed. Also, if the leaf was steady and air was then passed, the leaf slowly rose during a period of ten minutes and usually over about five small scale divisions. This result is probably closely connected with the observations made by Schlundt and Moore<sup>1</sup> in a somewhat similar case, and discussed by Randall<sup>2</sup> in a later paper. Readings were made only after the maximum point was reached.

The electroscopes was standardized by using an acid solution of a thorium mineral in which the disintegration products are in equilibrium. In the present case an analyzed specimen of thorianite was used. A flask containing distilled water, to which a certain volume of the standard thorianite solution was added, was substituted for *A* after first boiling to get rid of the radium emanation. The effect on the electroscopes of the emanation from a known quantity of thorium

could therefore be observed and compared with the results obtained from the soil solutions under similar conditions after the leak was deducted in each case.

In order to test the accuracy of the method, different thorianite solutions of known strength were used and the results compared. For example, 10 cc. containing 0.0021 gram thorium metal gave (leak deducted) a drop of twelve divisions per hour. 40 cc. of the same solutions gave a drop of 47.8 divisions per hour.

The results obtained are shown in Table III.

TABLE III

	Depth	Thorium gram $\times 1000$ per gram of soil
Durham sandy loam	10"–16"	5.4
Norfolk sandy loam	0"–14"	3.3
Decatur clay loam	4"–36"	5.6
Hagerstown loam	8"–36"	4.02
York silt loam	0"–8"	4.37

The results are not numerous enough to justify any conclusions as regards the relative amounts of thorium in the soils and subsoils. Comparing them with Joly's results on rocks, they seem to indicate that soils contain more thorium than most rocks, the average of the above results being much higher than the average of Joly's results, *viz.*,  $1.58 \times 10^{-5}$  gram per gram of rock. The figures are also higher than those obtained by Blanc for Roman soils.<sup>1</sup>

Strutt<sup>2</sup> has shown that the amount of radium in the earth's crust is more than sufficient to account for its internal heat. He did not take into account the thorium present. Averaging the amount of radium in the soils and subsoils and reducing this back to the uranium content, it can readily be seen that the amount of uranium present is about 10 per cent that of the thorium. While it is difficult to state just to what extent the thorium assists in maintaining the earth's internal heat, the effect must at least be appreciable.

The small variation in the amount of thorium in the five samples tested is noteworthy.

My thanks are due to Dr. Frank K. Cameron, Chief of the Division of Physical and Chemical Investigations, Bureau of Soils, for many courtesies extended during the progress of this investigation.

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## PARTIAL AND INTERMITTENT COMBUSTION OF GAS

BY E. E. SOMMERMEYER  
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### COMBUSTIBLE, INFLAMMABLE AND EXPLOSIVE MIXTURES

A *combustible mixture* is usually defined as a mixture of a composition such that if any part of it is raised to its ignition temperature a reaction between the components will become self-sustaining and will extend to all parts of the mixture; an *inflammable mixture* as a mixture of a composition such that if it is ignited at any point a visible flame will spread throughout the entire mixture; an *explosive mixture* as a mixture of a composition such that if a portion of it is raised to its ignition temperature an explosive reaction will

<sup>1</sup> *Trans. Am. Electrochem. Soc.*, **8** (1905), 292.

<sup>2</sup> *Ibid.*, **21** (1912), 463.

<sup>1</sup> *Phil. Mag.*, **13** (1909), 146–148.

<sup>2</sup> *Proc. Roy. Soc.*, (A) **77** (1906), 472–485.

take place throughout the entire mass. Given a sufficiently large volume of gas any mixture which is combustible or inflammable is also explosive.

With the combustion once started any one of three things is possible: The reaction may decrease in rapidity; it may remain constant; or it may increase in rapidity. An exactly constant rate of reaction is so rare that it may be disregarded as a possibility and the reaction may be expected either to accelerate or to decrease in velocity. If it accelerates an explosion will occur, provided a sufficiently large volume of gas is present. If it decreases, the combustion will die out and the gas, practically speaking, will be incombustible or at least only partially combustible.

#### DATA ON THE COMPOSITION OF COMBUSTIBLE AND EXPLOSIVE MIXTURES

The data in the literature regarding the lower limits of combustible and explosive mixtures of gas with air or with oxygen differ greatly. As an illustration, Hempel<sup>1</sup> gives the lower limit of combustible mixtures of hydrogen with air as from 5 to 6 per cent. Most other authorities give from 9 to 10 per cent. Techlu<sup>2</sup> gives the lower limits of an explosive mixture of methane with air as 3.2 per cent. Burrell<sup>3</sup> gives 5.5 per cent. Most other authorities give about 6.0 per cent. In comparing such widely different values one is at a loss as to the real facts. That differences of such magnitude are due to errors of manipulations on the part of some of the experimenters is hardly probable and they are rather to be ascribed to differences in conditions and in methods of work.

Some of the more probable factors contributing to these differences in experimental results are: (1) Impurities in the gases with which the experiments were performed. (2) Differences in the initial temperature of the gas. (3) Differences in the initial pressure of the gas. (4) Differences in the volumes of gas used. (5) Differences in method of ignition. (6) Differences in the design or style of the containers.

The recorded results, unless otherwise noted, were presumably obtained by starting at ordinary laboratory temperature and at atmospheric pressure, and it is hardly possible that any large amounts of unknown impurities were present in the gas mixtures used. It would therefore appear that no great discrepancies in results are to be explained by any or all of the first three sources of error, and large variations are more probably to be explained as due to the latter three. By varying these conditions the writer, as will be shown later in this paper, obtained results, which, while they are not entirely concordant, do tend to suggest reasons for the different values given for combustible and explosive mixtures.

#### EXPERIMENTS TO TEST THE INFLUENCE OF VOLUME OF GAS, METHOD OF IGNITION AND STYLE OF CONTAINER

In the experiments described in this paper the following volumes of gas mixtures were used:

<sup>1</sup> "Gas Analysis," Hempel.

<sup>2</sup> *J. prakt. Chem.*, **75** (1907), 212.

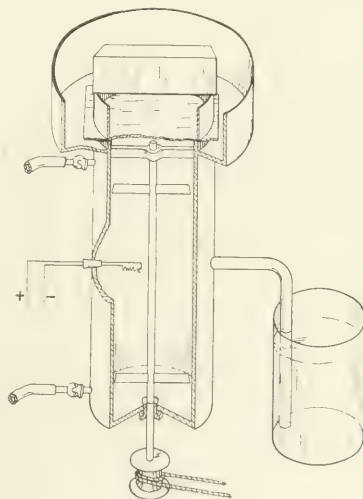
<sup>3</sup> *This Journal*, **5** (1913), 181.

CONTAINER				
Dimensions			Vol. cc.	Condition of experiment
Diam. Cm.	Length Cm.	Kind		
		Glass flask	145	Gas confined
8	26	Iron cylinder	1,300	Gas confined
9.5	29	Glass cylinder	2,100	Open at end
20	38	Iron cylinder	13,000	Gas confined
30	42	Iron cylinder	30,000	Gas confined

**DIMENSIONS OF THE CONTAINERS**—For the smallest container an ordinary short-neck globular CO<sub>2</sub> flask was used. This flask when stoppered had a capacity of 145 cc.

Each of the iron cylinders was fitted with an opening for the attachment of a water-sealed glass tube, with an opening for the insertion of a stopper carrying copper lead wires to which the wire fuses were attached and with two pet cocks or openings through which gas could be admitted or withdrawn and also through which water could be admitted to replace the gas withdrawn in sampling.

The accompanying cut of the 13,000 cc. cylinder shows the general arrangement of the stirring apparatus, glass delivery tube, paraffined paper-top, etc. The



projecting flange at the top is of galvanized iron and was used when it was desired to secure a water seal around paraffined paper. In experiments with mixtures rich enough to produce much of a reaction several thicknesses of paraffined paper were used and the necessary weight to hold the paper in place secured by using the ring above the paper as the fulcrum of a lever 5 or 6 feet long, upon the end of which weights were placed. In this way pressures equivalent to 700 or 800 pounds upon the head of the cylinder were readily secured.

The following methods of ignition were used:



- 1 0.5 to 0.75 cm. No. 34 platinum wire, heated to white heat
- 2 0.5 and 5 cm. No. 34 platinum wire, fused.
- 3 0.5 and 5 cm. No. 34 iron wire, fused.
- 4 5 cm. No. 34 tantalum wire, fused.
- 5 0.25 cm. spark from induction coil.
- 6 Oxygen-natural gas flame.

In performing the experiments with closed containers, two methods of observing whether or not a reaction took place were used.

(1) A bent glass tube was attached to the container, the open end of which dipped into water. With a vigorous reaction, gas was forced through the tube and bubbled up through the water. With a less vigorous reaction, the water in the tube was depressed through a noticeable distance.

#### DIAMETERS OF DELIVERY TUBES USED

145 cc. flask	3 mm. tube	13,000 cc. cylinder	12 mm. tube
1,300 cc. cylinder	6 mm. tube	30,000 cc. cylinder	12 mm. tube

(2) The mouth of the container was closed with paraffined paper, which, being flexible, was visibly moved by a slight reaction in the gas mixture, while with a vigorous explosion or combustion it was ruptured. This method was employed in some of the experiments with the cylinders of capacities of 1300 cc. and 13,000 cc.

In the experiments in which a delivery tube was used, any gas which escaped was replaced by water, and the analysis of the residual gas did not need to be corrected for dilution with air. The composition of the residual gas from experiments in which the cylinders were closed with paraffined paper was usually somewhat affected by dilution with air. There was more or less leakage of gas outward around the edge of the cylinder when the gas was subject to the pressure caused by combustion or explosion, and this was followed by a resultant leakage of air inward upon the cooling and contraction of the gas. The errors in the results caused by this leakage were, however, of minor importance and had no bearing on the general conclusions deduced from the analysis.

In using the 145 cc. flask no effort was made to mix the gas and air, as with this small volume diffusion was deemed sufficient to give a uniform mixture after a few minutes. In using cylinders containing 1300 cc., 2000 cc., and 30,000 cc., mixing was secured by inverting the cylinder ten or twelve times and allowing it to stand each time for a few seconds up to several minutes before reversing. In using a cylinder of 13,000 cc., mixing was accomplished by means of a pair of fan blades on a rotating shaft which was turned several hundred times before the ignition of the mixture.

The current used for heating the 0.5 to 0.75 cm. of No. 34 platinum wire to a white heat was obtained by using two 32 candle power carbon lamps in parallel. For fusing the platinum, iron and tantalum wires, three to four 32 candle power lamps in parallel were used. In the fusing of the platinum wire less than one calorie of heat was developed. In the fusion of the iron and tantalum wires slightly more heat may have been developed owing to some oxidation. In the experiments with the 13,000 cc. cylinder one calorie of heat would be sufficient to raise the temperature of the gas mixture only about 3° C.

All the experiments were performed at laboratory temperatures which varied for different days from as low as 18° C. to as high as 27° C. Some of the results obtained with the different methods of ignition and the different volumes of gas together with analyses of the resultant gases are as follows:

#### HYDROGEN AND AIR

WITH THE 145 CC. FLASK—Method of ignition, 0.5 cm. No. 34 platinum wire heated to white heat for 2 seconds. A blank on air under the same conditions gave a 5 cm. depression of water in the delivery tube.

##### RESULTS WITH DIFFERENT PERCENTAGES OF HYDROGEN IN AIR

Per cent hydrogen	Depression Cm.	Per cent hydrogen	Depression Cm.
4.5	10	6.0	20
5.0	15	7.1	70
5.5	20	8.2	Flask blown off of the stopper.

Turning on the current for two additional intervals of one second each gave further reactions as follows:

Per cent hydrogen	Depressions Cm.	Per cent hydrogen	Depressions Cm.
5.0	15 and 10	6.0	20 and 12
5.5	20 and 10	7.1	20 and 15

After the third ignition of the 5.5 per cent mixture, analysis of residual gas for oxygen showed that only 0.2 per cent of the oxygen had burned, equivalent to 0.4 per cent of hydrogen.

##### RESULTS WITH A 0.25 CM. SPARK FOR 0.5 SEC. FROM AN INDUCTION COIL

Per cent hydrogen	Depression Cm.	Per cent hydrogen	Depression Cm.
4.3		5.6	
1st spark.....	20	1st spark.....	25
2nd spark.....	20	2nd spark.....	25
3rd spark.....	5	7.0	
		1st spark.....	75
		2nd spark.....	50

WITH THE 1300 CC. CYLINDER—Method of ignition, fusion of 0.75 cm. of No. 34 iron wire. Extent of reaction noted by movement of paraffined paper on the head of the cylinder.

Per cent hydrogen	Result	Per cent hydrogen	Result
4.5	No visible reaction	7	Very fair reaction
4.6	Very faint reaction	8	Weak explosion
5.0	Fair reaction	9	Fair explosion, not violent
6.0	Fair reaction	10	Vigorous explosion

WITH THE CYLINDER WATER-SEALED, glass tube to allow the escape of gas, and an iron wire fuse, several experiments with 7.7 per cent hydrogen all gave vigorous reactions, gas being forced out through the water-seal. Analysis of the residual gas for oxygen showed that from 1.4 to 2 per cent of hydrogen had burned.

WITH THE 13,000 CC. CYLINDER, iron wire fuse and 6 per cent hydrogen, about 500 cc. of the gas were forced out through 20 cm. of water. An analysis of the residual gas for oxygen showed that about 0.5 per cent of hydrogen had burned. With 7.7 per cent hydrogen about 2 liters of gas were forced out of the cylinder. An analysis of the residual gas showed that 0.4 per cent hydrogen had burned. Ignition of the residual gas by means of additional fuses gave combustion reactions up to 10 fuses. Up to the fourth fuse the reaction produced forced gas out of the cylinder through 30 cm. of water. Using 0.5 cm. of No. 34 platinum wire heated to a white heat for two seconds, a 7.7 per cent mixture of hydrogen gave two distinct reactions, the gas escaping through 20 cm. of water in two closely succeeding but distinctly separate portions. Analysis of the residual gas showed that 1.6 per cent of hydrogen had burned

Using a spark from the induction coil for about 0.1 second, a 7.7 per cent mixture of hydrogen gave a very vigorous reaction, several liters of gas being forced out of the cylinders. Analysis of the residual gas indicated that 0.8 per cent of hydrogen had burned. With 7.6 per cent hydrogen and with the spark left running for several seconds, three distinct reactions were observed.

WITH THE 30,000 CC. CYLINDER and iron wire fuse, mixtures of from 7.3 to 7.7 per cent hydrogen gave fair reactions as was indicated by the forcing of gas out of the cylinder through water. Analysis of the residual gas showed that only about 0.4 per cent of hydrogen had burned. A 7.7 per cent mixture ignited with a dozen successive fuses gave reactions each time; up to the ninth fuse, the reaction forced gas out of the cylinder through 18 cm. of water; whereas, the burning of a fuse in the cylinder filled with air gave no visible depression.

#### NATURAL GAS AND AIR

Natural gas from the Columbus, Ohio, city mains was used. This gas on analysis was found to consist of approximately 85 per cent of methane and 15 per cent of ethane.

WITH THE 145 CC. FLASK, a 5 per cent mixture of natural gas and air gave no visible reaction when ignited with 0.75 cm. of No. 34 platinum wire heated to a white heat.

Per cent natural gas in air	Spark	Time of Depres- sion Seconds	Per cent natural gas in air	Spark	Time of Depres- sion Seconds
4.4	1st	1 30	5.6	1st	1 1/2 75
	2nd	1 20		2nd	2 60
	3rd	1 20		3rd	2 50
5.0	1st	1 30		4th	4 75
	2nd	1 25	Blank on air	1st	1 10
				2nd	5 20

On several other tests with mixtures containing from 5.7 per cent to 5.2 per cent of gas and using a spark for 0.5 second, the flask was blown from the stopper.

WITH THE 1300 CC. CYLINDER—Method of ignition, fusion of from 0.5 to 0.75 cm. No. 34 platinum or iron wire. A 4.6 per cent mixture of gas and air produced a 4 cm. depression. A blank on air produced a depression of 1 cm.

A mixture of 4.8 per cent of gas and air produced vigorous reactions, gas being forced out against a pressure of 5 lbs. per square inch. Analysis showed the presence of 2.6 per cent  $\text{CO}_2$ , indicating that about one-half of the gas had been burned. With paraffined paper closing one end of the cylinder, and with a 0.75 cm. platinum wire heated to fusion, a fair reaction was detected with as low as 4.6 to 4.7 per cent mixtures of natural gas and air. Mixtures of from 4.9 to 5 per cent of gas and air gave fair combustion, a distinct flame being visible.

RESULTS WITH 5 CM. NO. 34 IRON AND PLATINUM FUSES—Blanks on fuses in air gave for the iron fuse a depression of 12 cm. and for the platinum fuse a depression of 10 cm. A 4.3 per cent mixture of gas and air gave a depression of 30 cm. with an iron fuse and a depression of 20 cm. with a platinum fuse. Using a 5 cm. tantalum wire fuse, blanks on fuse in air gave a depression of 12 cm. Mixtures of 4.3 per cent and 4.4 per cent of gas and air gave depressions of 40 and 50 cm., respectively.

WITH THE 13,000 CC. CYLINDER, iron wire fuse, paraffined paper head on cylinder.

With a 4.7 per cent mixture of natural gas, no visible reaction was produced.

With a 4.8 per cent mixture of natural gas, a faint reaction was produced.

With a 5 per cent mixture of natural gas, a fair reaction was produced.

With a 5.2 to 5.3 per cent mixture of natural gas, a fair reaction was produced, the paper head of the cylinder being scorched by the heat of the combustion.

Tests after combustion on the residual gas from mixtures containing 5.2 and 5.3 per cent of natural gas gave results for  $\text{CO}_2$  of from 0.8 to 1.2 per cent, indicating that approximately this amount of the natural gas had burned. These values are, however, somewhat too low, owing to the leaks inward of air after combustion. This is shown by the more complete analysis after combustion of the residual gas from a 5 per cent mixture of natural gas, upon which values were obtained as follows:  $\text{CO}_2$  1.4,  $\text{CH}_4$  2.7,  $\text{C}_2\text{H}_6$  0.6 per cent.

On the basis of natural gas consisting of approximately 85 per cent  $\text{CH}_4$  and 15 per cent  $\text{C}_2\text{H}_6$  the original mixture contained 4.25 per cent of  $\text{CH}_4$  and 0.75 per cent of  $\text{C}_2\text{H}_6$ . On the residual gas after combustion the  $\text{C}_2\text{H}_6$  is 0.15 per cent lower and the  $\text{CH}_4$  1.55 per cent lower than in the original mixture. If these amounts burned to  $\text{CO}_2$  the  $\text{CO}_2$  formed would equal  $1.55 + 0.30 = 1.85$  per cent as against 1.4 per cent of  $\text{CO}_2$  actually found. This corresponds to a dilution of the original mixture with approximately 25 per cent of air.

#### EFFECT ON IGNITION BY A WHITE HOT PLATINUM WIRE COMPARED WITH IGNITION BY FUSION OF THE WIRE

A 5.1 per cent mixture with 0.75 cm. No. 34 platinum wire heated to a white heat for two seconds gave no visible reaction, but upon turning on additional current and fusing the wire, a fair reaction occurred, about 500 cc. of gas being forced out of the cylinder. Analysis of the residual gas for carbon dioxide and oxygen indicated that only about 0.2 per cent of the natural gas had burned.

The ignition of the gas by fusion of the wire and its failure to ignite from the wire raised to a white heat shows very clearly the great effect of a very high temperature of ignition upon the starting of the reaction.

#### EXPERIMENTS WITH THE OXYGEN-NATURAL GAS FLAME AS A SOURCE OF IGNITION

Mixtures of natural gas and air, and hydrogen and air were collected over water in the 2100 cc. glass cylinder which was then closed with a glass plate. The gases were mixed by inverting the cylinder a number of times, and then with the cylinder inverted, it was quickly slipped off of the glass plate which closed it and passed over the oxygen gas flame, the flame being in the cylinder for about one-half second. This flame was about 10 cm. long and consumed about 3 cc. of natural gas per second. With natural gas no visible combustion was obtained with 5 per cent of gas, but with a 5.5 per cent mixture the combustion was quite evident, a blue flame spreading slowly throughout the cylinder. With hydrogen no reaction was detected with a 6 per cent mixture. With a 7 per cent and a 7.7 per cent mixture no visible flame was noticeable but an appreciable reaction was indicated by the deposit of a film of moisture upon the cold sides of the cylinder. That an appreciable reaction is started by the oxygen-natural gas flame in mixtures of natural gas and air lower than 5.5 per cent is shown by the following experiments upon different mixtures of gas and air in the 13,000 cc. cylinder: In making the experiments a cork was removed from a 2 cm. opening in the side of the cylinder and the tip of the flame inserted into the cylinder for from 1 to 3 seconds. Considerable reaction occurred as was shown by the rapid swelling of the paraffined paper top used to close the cylinder and by the rapid escape of gas through the opening in which the flame was inserted. In each case the effect was greater than that which was produced in blank tests upon the cylinder filled with air. But in the mixtures used no violent reaction occurred. The extent of the reaction was approximately determined by analysis of the residual mixtures for  $\text{CO}_2$ . The flame used 3 cc. of natural gas, and produced approximately 3 cc. of  $\text{CO}_2$  per second; or in the 13,000 cc. mixture less than 0.03 per cent of  $\text{CO}_2$  per second was added from this source. The results obtained upon the residual mixtures were as follows:

Per cent of natural gas in mixture	Time of flame in cylinder Seconds	Per cent CO <sub>2</sub> in resultant mixture	CO from flame	Per cent of CO <sub>2</sub> from gas burned	Approx- imate cc. of natural gas burned
4.4	5	1.0	0.15	0.85	100
4.0	5	1.0	0.15	0.85	100
3.2	3	0.6	0.10	0.50	60
2.0	4	0.3	0.10	0.20	25

These results all show appreciable combustion around the flame. This combustion was in all cases greater than is shown by these results on account of the expansion of the gas and the dilution of the remaining gas with air upon contraction before the gas was sampled and analyzed. That partial combustion of such mixtures occurs is shown by the well known lengthening of a lamp flame in air containing fire damp.

#### ANALYSIS OF RESULTS

The experiments here recorded show conclusively that with a high initial ignition temperature a reaction may start in a gas mixture, which, as a whole, may be incombustible because the heat of combustion is not sufficient to maintain the temperature at the kindling point. Hence all of the mixture will not burn although the reaction may be sufficiently extensive as to make the mixture appear to be combustible or explosive. With the source of high temperature employed to cause ignition acting for only a very brief interval of time, as during the fusion of platinum or iron wire, the resultant reaction quickly ceases but not until a combustion of gas has occurred, the heat of which is in some cases equivalent to hundreds of time the energy required to heat the platinum or iron fuse. The heat liberated by the fusion of 0.75 cm. of No. 34 platinum or iron wire is only a fraction of a calorie. In a 7.7 per cent mixture of hydrogen this fuse, as has been shown, causes a combustion of 0.4 per cent of hydrogen in a 30,000 cc. mixture or of 120 cc. of hydrogen. This liberates about 300 calories of heat. In the smaller containers a greater percentage of the hydrogen was burned. For example, in the 1300 cc. cylinder as high as 2 per cent of hydrogen burned or only 26 cc. From this it would appear that when the combustion is started from a source of very high temperature, more gas is burned in a large volume of mixture than in a small volume, but that the greater percentage of the gas is burned in the smaller mixture. This is at least partially accounted for by the cooling of the gas by the walls of the container, especially where small volumes are burned; but with large volumes of gas, as in the case of the two large cylinders holding 13,000 and 30,000 cc., respectively, this would be of little effect; and in a room full of gas the effect would be entirely negligible. With a continuous source of high temperature, as with a white hot wire, a lamp flame or a running electric spark, the reaction produced may be intermittent. The gas immediately around the point of ignition burns and expands, and combustion around that point ceases until another portion of the mixture of gas and air has replaced the expanded gas and products of combustion, whereupon another reaction takes place resulting in a series of combustions or explosions.

The limits of appreciable ignition or combustion of hydrogen and of natural gas in air vary with the volume of gas used, the source of ignition and the style

of the container. In a 2000 cc. open cylinder the lower limit obtained for natural gas is about 5.5 per cent. With hydrogen the lower limit for very appreciable ignition was above 7 per cent. In a closed container the lower limit for natural gas using 0.5 cm. of No. 34 platinum wire heated white hot, was over 5 per cent. With a 0.5 cm. platinum or iron wire fused the lower limit obtained was 4.7 to 4.8 per cent. With a 5 cm. No. 34 wire fused the lower limit obtained was about 4.3 per cent. With a 5 cm. No. 36 tantalum wire fused the lower limit was about 4.3 per cent. With a 0.25 cm. spark from an induction coil the lower limit of appreciable reaction was about 4.3 per cent. With closed containers, 6 to 7 per cent mixtures of hydrogen and air gave vigorous reactions with 0.5 cm. platinum or iron wire fuses. With the electric spark, mixtures as low as 5 per cent gave very noticeable reactions, and faint reactions were obtained with mixtures as low as 4.3 to 4.6 per cent.

For the same percentage of gas and the same method of ignition, small volumes of gas gave more vigorous reactions than large volumes, but in total amount of gas burned, the combustion obtained in large volumes was greater than that obtained in small volumes.

With smaller containers, or with a more powerful spark, or a longer wire fuse, undoubtedly very appreciable reactions can be obtained with mixtures of lower percentages than those given, but with ordinary sources of ignition, large volumes of gas will not react appreciably unless the mixture is richer in gas than the lowest limits obtained in these experiments. However, the thermal calculations<sup>1</sup> based on 850° and 700° as the ignition temperature required for explosive mixtures of natural gas and of hydrogen with air indicate that mixtures of natural gas in excess of 2 per cent and of hydrogen in excess of 5.9 per cent are potentially explosive if conditions favorable to the reaction are present. Some of these conditions, in addition to a vigorous source of ignition, are unusually high in initial temperature of the mixtures of gas and air, presence of fine combustible dust, and an increase in the pressure of the mixture.

The results of these experiments indicate that a comparatively small excess of hydrogen above the theoretical requirement is necessary to produce a vigorous reaction. Natural gas or methane, on the other hand, ignites with such difficulty that, with ordinary methods of ignition, an appreciable reaction does not occur unless a very large excess of gas is present above that required by the thermal calculation.

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#### WOOD DISTILLATION UNDER DIMINISHED PRESSURE A CONTRIBUTION TO THE PROBLEM OF UTILIZATION OF WOOD WASTE

By MAXWELL ADAMS AND CHARLES HILTON

Received Dec. 27, 1913

The rapid decrease in the supply of long leaf pine available for the production of turpentine and the immense waste of resinous wood in the lumber indus-

<sup>1</sup> THIS JOURNAL, 6, 191.



try throughout the country has stimulated chemists in an effort to devise some practical method for the extraction of wood turpentine from stumps, lapwood and mill waste. According to the Report of the Bureau of Chemistry<sup>1</sup> there are more than five million cords of waste wood left annually in the forests in the lumbering of resinous woods. The amount of waste is greatly increased when we add to this the dead and fallen timber of the uncut forest.

The methods for extracting turpentine from resinous wood, so far proposed, may be classed under four heads: 1. Destructive distillation, with or without steam. 2. Steam distillation. 3. Distillation with hot rosin. 4. Extraction with volatile solvents. These methods have all been tried out with varying degrees of success, but it is somewhat doubtful if any of them have developed beyond the experimental stage. The commercial success of any method will depend largely upon the demand for the by-products, and the utilization of all parts of the wood. The steam distillation process in conjunction with the manufacture of paper pulp appears promising<sup>2</sup> and the destructive distillation method has often been successful where charcoal, creosote and rosin oils are in demand.

The method described in this paper proposes to improve the ordinary destructive distillation process by controlling the temperature and diminishing the pressure at which the distillation takes place, thereby avoiding superheating and at the same time vaporizing the turpentine at a temperature below which it will not decompose.

According to Violette,<sup>3</sup> when wood is carefully heated to 150° C. water only is distilled, and decomposition begins at about 160° C. These results will probably vary with the kind of wood. In order to determine the effect of heat upon the variety of wood to be used in later experiments a sample of western yellow pine, *Pinus ponderosa*, was placed in a flask immersed in a sulfuric acid bath and heated very slowly. Care was taken that the temperature of the bath did not exceed that of the interior of the flask by more than five degrees. At 94° (the barometric pressure of the laboratory being 645 mm.) distillation of water and turpentine begins. When kept at 160° C. for several hours the wood turns brown, and above this temperature there is abundant evidence of decomposition. Gaseous decomposition begins when a temperature of 220° C. is reached.

Although pure turpentine distils at 155-6°, yet when dry wood is heated only a small percentage of the turpentine present is driven off when decomposition begins. This is explained by the fact that ordinary pitch as it occurs in wood is a solution of rosin and various waxes in turpentine; when a substance is dissolved in a liquid, the vapor pressure of the solvent is lowered at all temperatures, and the solution must therefore be heated to a higher temperature than would be required for the pure solvent, before distillation begins.

The rosin is not volatile; as the turpentine distils and the solution grows more concentrated, the vapor pressure is lowered, and the boiling point is correspondingly raised, until the temperature of decomposition is reached, and a large part of the turpentine is destroyed before it is vaporized. The presence of water in the wood, however, adds a factor which partly counterbalances this, and lowers the boiling point

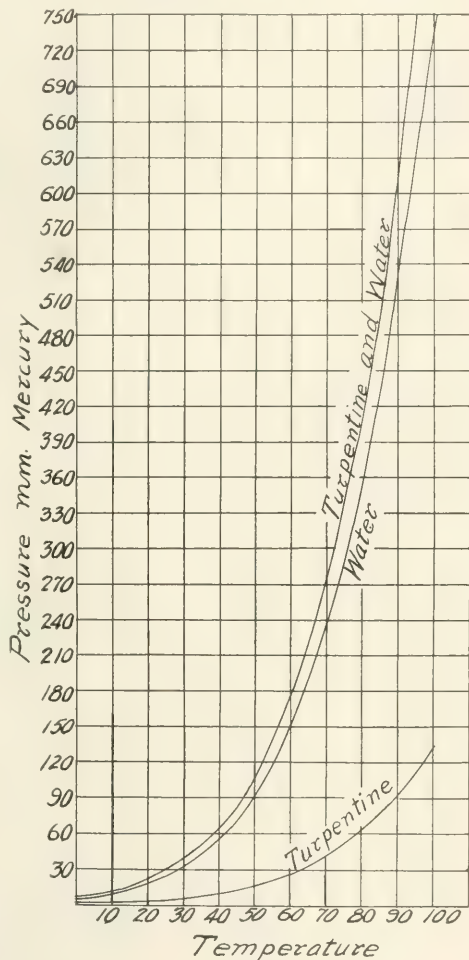


FIG. 1.

of the turpentine in the mixture. According to the law of Regnault<sup>1</sup> for immiscible liquids, water and turpentine will distil at the temperature at which the sum of their vapor pressures is greater than atmospheric pressure, neither influencing the vapor pressure of the other. The quantity of each liquid found in the distillate will be proportional to their vapor densi-

<sup>1</sup> Bull. 159.<sup>2</sup> Bur. of Chem., Bull. 159.<sup>3</sup> Sadtler's "Industrial Organic Chemistry," p. 348.<sup>1</sup> Pogg. Ann., 93, 537.

ties and can be calculated by means of Avogadro's law.

A mixture of water and turpentine (the barometric pressure in the laboratory being 652 mm.) boils at

If we consider the gram molecular volume at 93° as being  $\frac{22.4 (273 + 93)}{273}$  liters, and assume turpentine to consist of pinene with a molecular weight of 136,

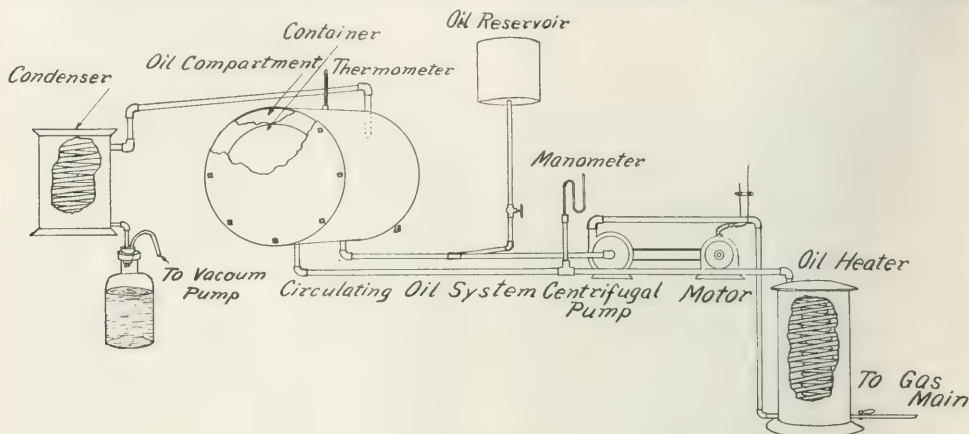


FIG. 2

93° C. Water at this temperature has a vapor pressure of 588 mm. The remaining 64 mm. pressure must be due to the turpentine. The vapor pressure of

then the mixed vapors will be found to consist of  $\frac{18 \times 588}{652} = 16.2$  parts of water vapor and  $\frac{136 \times 64}{652} = 13.3$  parts of turpentine vapor. The ratio of the weight of water to turpentine in the vapor is approximately 100 to 80, and this is also the ratio of their weights in the distillate.

The density of turpentine is 0.85, therefore the volume of water and the volume of turpentine are practically equal when the distillation takes place at atmospheric pressure, but the proportion of turpentine in the distillate should be considerably increased when the distillation is carried on under diminished pressure, as is shown by the examination of the vapor pressure curves in Fig. 1.

The vapor pressure of turpentine at 30° is 6.9 mm. and that of water at the same temperature is 31.5 mm.; a total of 38.4 mm. By applying the preceding method of calculation we find that the mixed vapors at 30° will consist of  $\frac{18 \times 31.5}{38.4} = 14.7$  parts of water

vapor and  $\frac{136 \times 6.9}{38.4} = 24.4$  parts of turpentine vapor.

Thus the amount of turpentine vaporized is practically double that of the water, when the distillation takes place at 38 mm. pressure. These results are confirmed by experiment.

When we apply the steam distillation method to the extraction of turpentine from wood, the proportion of turpentine is very much diminished, and the distillation temperature is considerably higher, due to the presence of dissolved resins, which have greatly diminished the vapor pressure of the turpentine. Experiments show that, under the most favorable conditions, 15 parts of water remove 1 part of turpentine. The proportion of water, however, varies

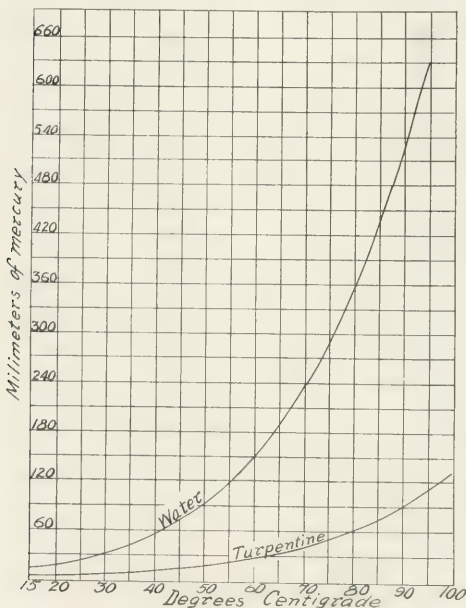


FIG. 3

pure turpentine<sup>1</sup> shows that a mixture of it and water should boil at about 91° C. The slight solubility of each in the other doubtless lowers the vapor tension of both.

<sup>1</sup> "Smithsonian Physical Tables," p. 126

widely, depending upon the rate of distillation and the size of the wood chips.

TABLE I

Number of fraction	Temp. of oil bath °C.	Temp. of dist. flask °C.	Expt. No. 1 Press. normal		Expt. No. 2 Press. 35 mm.	
			Vol. turp. Cc.	Vol. water Cc.	Vol. turp. Cc.	Vol. water Cc.
A.....	100-150	40-94	0.0	0.0	7.2	3.1
B.....	150-190	94-120	5.3	4.2	2.8	2.2
C.....	190-200	120-140	4.3	3.2	2.5	1.9
D.....	200-220	140-160	1.4	0.6	1.1	1.5
E.....	220-270	160-180	1.8	1.6	2.1	3.0
F.....	270-300	180-200	2.3	4.0	4.6	3.2
G.....	300-330	200-220	3.1	6.1	6.4	4.1

By decreasing the pressure, according to the preceding theoretical considerations, the amount of the turpentine produced at a given temperature should be

TABLE II

Expt. No. 3, press. normal Expt. No. 4, press. 80 cm.

Frac.	Dist. temp. °C.	Expt. No. 3, press. normal		Expt. No. 4, press. 80 cm.	
		Vol. crude turp. Cc.	Sp. gr. crude turp.	Vol. refined turp. Cc.	Vol. refined turp. Cc.
A.....	Up to 220	570	0.855	501	920
B.....	220-250	220	0.884	176	320

considerably increased. Accordingly, an ordinary distilling apparatus, with a capacity of about 200 grams of wood shavings, was fitted up and attached to a

TABLE III

Variety of wood used	Frac.	Temp. of distil. °C.	Time of oil of distil.	Vol. of ref. turp. obt. at press. Cc.	Vol. of refined turp. obt. at 80 cm. press. Cc.
Pinus Monophylla...	A	Up to 220	1 hr 30 m.	180	250
Pinus Monophylla...	B	220-250	1 hr.	108	150
Pinus Jeffreyi...	A	Up to 200	1 and 1/2 hr.	100	150
Pinus Jeffreyi...	B	200-220	1 hr.	95	105
Pinus Jeffreyi...	C	220-250	1 hr.	80	75

pump capable of maintaining the apparatus at a pressure of 35 mm. To avoid superheating, the distilling flask was placed in an oil bath. A sample of thoroughly dry, western yellow pine, fairly rich in pitch, was cut into chips, which would pass through

represent the extremes of variation. Time being an important factor in determining the quantity of distillate obtained from wood, the temperature was raised 20° in approximately 30 minutes. Time and temperature thus being the same in both experiments, the variation in the amount of distillate secured in the different fractions must depend upon the pressure. The distillate coming over below 160°, the temperature at which the decomposition of wood begins is 20 per cent greater under diminished pressure than that distilling at ordinary pressure. The fractions coming over, both above and below 160°, under diminished pressure are much lighter in color than those distilling at atmospheric pressure. When the temperature reaches 220° gaseous decomposition begins and diminished pressure can no longer be maintained.

In order to repeat the above experiments on a larger scale, a double-walled retort, capable of holding about 25 kilos of wood, and similar in form to the one described by Pritchard<sup>1</sup> was constructed.

The plan of the apparatus is shown in Fig. 2. Oil is passed through copper coils heated in a gas flame. The hot oil is forced to circulate through the outside jacket of the retort by means of a small centrifugal pump. By this means the temperature is under complete control and superheating is avoided. The door, through which the retort is filled, is closed with a ground joint, and made air-tight by means of set screws. The vapors from the retort pass through a condenser into a receiver, which is connected with a Geryk vacuum pump, capable of maintaining the entire apparatus, when in operation, at a pressure of 80 cm. The oil used to conduct the heat to the retort has a flash point of over 300° C. and is capable of withstanding a temperature of 400° C. without cracking, when heated in a closed vessel under pressure.

To test the efficiency of the method, a sample of western yellow pine was cut into pieces one foot long and about one inch in diameter, thoroughly dried, divided into three equal portions of 22 kilos each, and subjected to the following treatment: I. Distilled in a retort by direct heat, without any attempt at temperature control or fractional separation of

TABLE IV

No. of fraction	Temperature of retort °C.	Vol. in cc. of pyro. acid obtained	Sp. gr. of pyro. acid	Per cent wood alcohol in pyro. acid	Per cent acetic acid in pyro. acid	Vol. in cc. of tar obtained	Sp. gr. of tar	PER CENT TAR DISTILLING			Per cent pitch residue in flask	Per cent water in tar
								below 180° C.	between 180°-240°	between 240°-320°		
A.....	160-200	1275	1.002	0.49	0.64	835	0.855	83.5	3.0	2.1	9.6	1.8
B.....	200-240	560	1.013	0.91	1.13	280	0.884	62.5	4.2	5.0	27.2	2.1
C.....	240-270	885	1.041	1.43	4.01	590	0.930	39.6	12.8	14.6	31.1	1.9
D.....	270-280	675	1.053	1.65	5.06	420	0.953	25.2	16.9	19.2	35.8	2.9
E.....	280-290	1045	1.061	2.15	5.48	925	0.993	13.9	12.5	16.3	44.7	2.8
F.....	290-300	975	1.070	3.68	4.54	1000	1.025	10.1	12.2	14.3	61.4	2.0
G.....	300-360	920	1.073	2.67	2.65	960	1.032	7.4	11.2	13.8	65.3	2.3

a half inch mesh. The sample was thoroughly mixed and 175 grams were used in each experiment, the results of which are given in Table I.

On account of the difficulties of heat control there was some variation in the oil bath temperatures of Experiments 1 and 2. The numbers in Column 2

the crude distillate. II. Distilled in an oil-jacketed retort under atmospheric pressure. III. Distilled in an oil-jacketed retort under a pressure of 80 cm.

Method No. I yielded 1606 cc. of tar from which was extracted 424 cc. of a light brown, ill smelling,

<sup>1</sup> THIS JOURNAL, 4, 338.



TABLE V

Variety of wood used in the distillation	Vol of pyroligneous acid in liters	Per cent wood alcohol in pyro. acid	Per cent acetic acid in pyro. acid	Vol of tar in liters	Per cent turpentine oil in tar	Per cent creosote oil in tar	Per cent mixed heavy oil in tar	Per cent pitch in tar	Per cent water in tar	Kilos of charcoal
Sugar pine	9.8	0.52	2.6	1.26	8.5	9.0	15.7	56.1	10.2	3.64
Yellow pine	12.4	0.55	2.2	2.09	10.6	6.2	20.2	46.9	6.5	4.32
Stump wood pine	10.9	0.57	2.4	3.80	18.1	9.0	20.4	50.4	2.4	4.09
Red fir	11.1	0.48	1.8	1.78	16.1	7.8	18.4	47.1	11.2	5.03
Silver fir	10.1	0.51	2.1	1.23	11.2	11.0	18.4	53.1	8.4	4.77
Millstaves	9.6	0.61	2.7	1.81	9.2	8.1	20.7	48.8	11.8	4.53
Sage brush	9.4	3.54	11.53	1.94	..	16.2	14.7	15.6	48.0	7.8

wood turpentine, distilling below  $170^{\circ}$ . The results obtained from Experiments 3 and 4 are given in Table II.

Sample A is almost colorless and easily purified by distillation, but Sample B contains impurities, which can be removed only by alternately washing with caustic soda and sulfuric acid and redistilling.

Experiments 3 and 4 were repeated, using samples of other kinds of wood with results given in Table III.

From the above results it is evident that the yield of turpentine under diminished pressure is from 10 to 20 per cent higher than that obtained at ordinary pressure, using the same method of heat control, while it is double that obtained by the common destructive distillation method. In addition to this the quality of the product is much improved. If, however, as shown by a number of experiments in this laboratory, the wood used is green, and contains water in large excess of the volume of turpentine, then the process becomes one of steam distillation and the diminished pressure, while bringing the distillate over at a lower temperature, produces no decided increase in the total yield of turpentine.

The samples of purified wood turpentine, obtained from each of these varieties of wood, is water white and looks like ordinary spirits of turpentine, but they differ from it, and from each other, in odor and optical properties. They are under examination in this laboratory in an effort to identify the various terpenes present.

When the temperature of the retort reaches  $250^{\circ}$ , the volume of the gases given off is so great that the pump is no longer efficient in reducing the pressure, and distillation under diminished pressure becomes impossible. In order, however, to determine the total amount and the properties of the different products obtained at various temperatures from western yellow pine, 22 kilos of a sample of dry "light wood" were submitted to distillation in an oil-jacketed retort with results tabulated in Table IV.

After the distillation there remained 7.8 kilos of charcoal. The time for the distillation of each fraction was one and a half hours and the temperature was raised at almost uniform rate.

There are many varieties of wood indigenous to the Pacific coast, concerning the distillation products of which there is no published data. Samples of a number of these varieties, as they occur in the lumber districts of the Sierra Nevada Mountains, were submitted to destructive distillation. The results obtained are set down in Table V. The amount of wood used in each experiment was 25 kilos, and the methods

used in the examination of the distillate are those described in Allen's "Commercial Organic Analysis."

#### SUMMARY

The above experiments show that:

I. The western conifers contain wood turpentine in commercial quantities.

II. Under favorable conditions a cord (4,000 lbs.) of yellow pine will yield 25 gallons of wood turpentine.

III. The yield of turpentine from a given sample of dry wood can be increased by distilling under diminished pressure.

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#### THE NATURE OF BASIC LEAD CARBONATE

By EDWIN EUSTON

Received February 24, 1914

In an article<sup>1</sup> "On the Composition of White Lead," reasons were presented for the assertion that white lead consists of a mixture of normal lead carbonate with a basic carbonate of lead of the composition  $\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ . The purpose of the present paper is to consider the nature of the combination of the components of this basic carbonate of lead. The existing assumption in text books on pigments is that, in basic carbonate of lead, the lead carbonate and the lead hydroxide are firmly united in actual chemical combination, but the results obtained in the experiments here to be mentioned indicate rather that the basic carbonate of lead should be considered as among those substances described by Zsigmondy<sup>2</sup> as mixtures of colloidal substances which can, under certain conditions, act as chemical compounds. "Not only<sup>3</sup> have colloid compounds or colloidal mixtures, in which two colloids are united, been erroneously described as chemical compounds, but so also have mixtures or adsorption compounds of crystalloids with colloids."

The fact that the lead hydroxide portion of basic lead carbonate is soluble in ammonium chloride solution but not in cane sugar solution, indicates that the lead hydroxide is not present in mere mechanical mixture and yet is not so firmly held as to be properly considered in chemical combination. Direct evidence that the basic carbonate of lead is an "adsorption compound" is afforded by the fact that, in more than fifty trials, various samples of white lead and of lead carbonate, when treated with basic lead acetate solution at room temperature by stirring or agitation, invariably with-drew lead hydroxide from the solution and correspond-

<sup>1</sup> THIS JOURNAL, March, 1914:

<sup>2</sup> "Colloids and the Ultramicroscope," N. Y., 1909, p. 68.

<sup>3</sup> *Ibid.*, p. 69.

ingly gained in weight. In composition the samples before treatment ranged from 12.0 to 16.3 per cent  $\text{CO}_2$ , and after treatment contained as low as 10.1 and 10.3 per cent  $\text{CO}_2$  in extreme cases. The extent of the reaction under uniform temperature conditions is dependent on the basicity of the lead acetate solution, on the relative amounts of the sample to be treated and of the available lead hydroxide in the solution, and on the duration of the treatment. Merely enough agitation is required to ensure uniform treatment. The process proceeds slowly, requiring, for example, six hours in one instance to enable a sample containing 14.7 per cent  $\text{CO}_2$  to join with enough lead hydroxide from the solution to reduce to 10.1 per cent  $\text{CO}_2$  in the final product. Excess of basic lead acetate in solution beyond the calculated amount is required for complete action, as the end point of the reaction is an equilibrium determined by the relative basicity of the solution and of the sample under treatment. With a sample containing both normal lead carbonate and basic lead carbonate this equilibrium can be disturbed in either direction at will by the addition of a further quantity of basic lead acetate solution or by the addition of neutral lead acetate solution. Samples prepared from lead carbonate in the manner described respond to the tests for basic lead carbonate to the extent that their analyses indicate.

To learn whether normal lead carbonate is unique in its ability to withdraw lead hydroxide from basic lead acetate solution, similar trials, using considerable excess of basic lead acetate solution, were then made with kaolin, commercial zinc oxide, basic zinc carbonate, whiting, precipitated calcium carbonate, precipitated barium sulfate and precipitated barium carbonate. The kaolin gained 10.6 per cent in weight by addition of lead hydroxide, and two different brands of zinc oxide gained only 0.6 per cent each. The other substances named formed compounds corresponding approximately to the following formulae:

Basic zinc carbonate became  $\text{ZnCO}_3 \cdot \text{Zn}(\text{OH})_2 \cdot 3\text{Pb}(\text{OH})_2$ .

Whiting became  $2\text{CaCO}_3 \cdot \text{Pb}(\text{OH})_2$ .

Precipitated  $\text{CaCO}_3$  became  $2\text{CaCO}_3 \cdot \text{Pb}(\text{OH})_2$ .

Precipitated  $\text{BaSO}_4$  became  $3\text{BaSO}_4 \cdot \text{Pb}(\text{OH})_2$ .

Precipitated  $\text{BaCO}_3$  became  $3\text{BaCO}_3 \cdot 2\text{Pb}(\text{OH})_2$ .

The calcium compounds and the barium sulfate compound were so lacking in opacity as to be worthless as pigments. The barium carbonate compound and the basic zinc carbonate compound showed marked improvement in density, in opacity, in brushing quality, and in rapidity of drying with linseed oil, in these respects closely resembling white lead. In tinting and spreading power the basic zinc carbonate compound equalled white lead, and the barium carbonate compound considerably exceeded it. These results show that other substances than normal lead carbonate form compounds with lead hydroxide from basic lead acetate solution, and that the lead hydroxide so combined tends to give to such compounds, in varying degree, characteristics as pigments heretofore ascribed only to white lead. Further similarity is shown by the lead hydroxide portion of the compounds being soluble in

ammonium chloride solution but not in cane sugar solution.

The slow withdrawal of lead hydroxide from basic lead acetate solution by normal lead carbonate to form basic lead carbonate, the like action of some other substances in forming lead hydroxide compounds, the similarity in some properties conferred by the lead hydroxide on these different compounds, and the fact that the lead hydroxide is present neither in mechanical mixture nor in true chemical combination, indicate that basic lead carbonate is an adsorption compound.

ESTON WHITE LEAD COMPANY, ST. LOUIS

## THERMAL REACTIONS IN CARBURETING WATER GAS PART I—THEORETICAL

By M. C. WHITAKER AND W. F. RITTMAN

Received April 13, 1914

Much careful scientific work has been done on the equilibria involved in the manufacture of uncarbureted blue water gas. In the combined processes of manufacturing and carbureting blue water gas according to present practice, few experiments have been made on the equilibria of the constituents to find out the effect of varying pressure, temperature and concentration conditions. In the technical literature of gas manufacture, one rarely finds a reference to the relationship which may exist between the spheres of reaction in the process. The natural conclusion has been that the water gas and oil gas reactions are separate and influence each other but little.

It is proposed to consider some of the factors in which the  $\text{H}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$  and  $\text{H}_2\text{O}$  of the blue water gas may affect the proportions of  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{H}_4$ ,  $\text{H}_2$ , etc., resulting from the cracking of the gas oil which is added. Likewise the influence of the gases coming from the oil on the percentage composition of the final gas mixture will be considered.

When the blue water gas or oil gas are manufactured in separate operations, hydrogen is the only gas which is found in the free state, in any quantity. But if the two gases, separately made, should be brought together at high temperature in a container such as a gas plant superheater, would there not be new equilibria to be satisfied? For example, might not the  $\text{CO}$  and  $\text{H}_2$  of one become  $\text{CH}_4$  and  $\text{H}_2\text{O}$  of the other, or *vice versa*? In case of these new equilibria there would, of course, be vital reactions between the gases of the two processes. In actual manufacturing practice, all the gases produced are in intimate contact at high temperature for the greater part of the manufacturing period, *i. e.*, while passing through the carbureter and superheater. Is it then correct to regard carbureted water gas as the result of two distinct reactions?

Equilibrium conditions tend to establish themselves both during the periods of initial cracking of the oil and the subsequent passage of the mixture through the carbureter and superheater. Gas oil itself can be "cracked" in a short distance, as has been shown in practically all laboratory experiments; in the laboratory the length of the cracking tube is usually a question of inches. It would seem on *a priori* grounds that the only important reason for the existence of the superheater is to enable the various

gases present to interact ("fix") and reach a favorable equilibrium.

This laboratory has begun a comprehensive study of the reactions and equilibria involved in water gas manufacture. While unable to cover the field in two years, it has come to a full realization of the importance of the investigation. The present paper will be confined to a theoretical consideration of the problem. Further papers will take up experimental data.

The problem has been attacked entirely from the point of view of physical chemistry, and from the standpoint of mass action and thermodynamics. In so doing, the mechanism of the reactions involved has not been seriously considered. The materials at the start, the final products desired, the energy transformations essential to bring the latter from the former, the temperature, the pressure and the concentration conditions favorable to the changes have had primary consideration.

Basing an experimental investigation upon the theoretical considerations evolved, we have been able, among other things, to establish the following results:

(1) Increase the yield of illuminants over the best results recorded in the literature by more than 100 per cent.

(2) Decrease the carbon deposited to less than 1 per cent, by weight, of the oil used.

(3) Make an oil gas in which 56 per cent of the fixed gases are illuminants.

These figures result from the application of conditions more favorable to the theoretical deductions than at present used in water gas manufacture. Conversely by applying conditions more unfavorable to the theory involved, and comparing the maximum yield under these conditions with a maximum yield obtained under ordinary conditions, it has been found possible to:

(4) Decrease the yield of illuminants by 25 per cent.

(5) Increase the carbon deposited to 51.5 per cent, by weight, of the oil used.

(6) Make an oil gas containing only 5 per cent total illuminants.

Further, it has been found possible to produce:

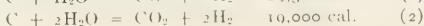
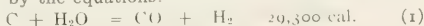
(7) A viscous tar of relatively high specific gravity containing naphthalene and anthracene; or

(8) A liquid "tar" of relatively low specific gravity resembling petroleum oil, and containing no naphthalene and anthracene.

In dealing with the problem, no single reaction can be considered exclusively by itself. All the reactions are vitally interrelated, though any single reaction, or set of reactions, may be extremely important as indicating a tendency. The experiments are designed to obtain the largest yield of hydrocarbons, and to eliminate, as much as possible, CO<sub>2</sub>, water vapor, deposited carbon, and tar vapors. The goal is to increase the yield of illuminants.

#### MANUFACTURE OF UNCARBURETED BLUE WATER GAS

The manufacture of blue water gas may be represented by the equations:



The two equations are combined by subtracting (2) from (1) in order to eliminate the carbon:



Equilibrium is established between these gases when

$$K = \frac{p_{CO} p_{H_2O}}{p_{CO_2} p_{H_2}}$$

where  $K$  represents the usual equilibrium constant; i. e., the value of the product of the partial pressures of CO and H<sub>2</sub>O divided by the product of the partial pressures of CO<sub>2</sub> and H<sub>2</sub>.  $K$  has a definite value for each definite absolute temperature.

For a practical illustration of the significance of equilibrium conditions in the manufacture of blue water gas, assume a theoretically ideal mixture consisting of 50 per cent H<sub>2</sub> and 50 per cent CO. Pass the two gases through a chamber heated to 700° C. (1290° F.) until they reach the equilibrium of this temperature; what are the resulting gases?  $K$  at this temperature is in the neighborhood of 0.32.



Under equilibrium conditions

$$\begin{aligned} \text{Let } X &= \text{volume CO}_2 \\ \text{then } X &= \text{volume H}_2\text{O} \\ 0.5 - X &= \text{volume H}_2 \\ 0.5 - 3X &= \text{volume CO} \\ 1 - 2X &= \text{total final volume} \\ \frac{X}{1 - 2X} &= \text{partial pressure CO}_2 & \frac{0.5 - X}{1 - 2X} &= \text{partial pressure H}_2 \\ \frac{X}{1 - 2X} &= \text{partial pressure H}_2\text{O} & \frac{0.5 - 3X}{1 - 2X} &= \text{partial pressure CO} \\ K &= 0.32 = \frac{p_{CO} p_{H_2O}}{p_{CO_2} p_{H_2}} = \frac{\left(\frac{X}{1 - 2X}\right)\left(\frac{X}{1 - 2X}\right)}{\left(\frac{0.5 - 3X}{1 - 2X}\right)\left(\frac{0.5 - X}{1 - 2X}\right)} = \frac{2X^2(1 - 2X)}{(0.5 - 3X)(0.5 - X)} \\ \text{Solving, } X &= 0.069 = 6.9 \text{ per cent} \\ 2X &= \text{gas lost in reaction} = 13.8 \text{ per cent} \\ \frac{X}{1 - 2X} &= \frac{0.069}{0.862} = 8 \text{ per cent CO}_2 \\ \frac{X}{1 - 2X} &= \frac{0.069}{0.862} = 8 \text{ per cent H}_2\text{O} \\ \frac{0.5 - 3X}{1 - 2X} &= \frac{0.293}{0.862} = 34 \text{ per cent CO} \\ \frac{0.5 - X}{1 - 2X} &= \frac{0.431}{0.862} = 50 \text{ per cent H}_2 \end{aligned}$$

Applying the above calculations to a mixture of 1,000 cu. ft. each of carbon monoxide and hydrogen, and assuming that no hydrocarbons are formed, there would be a net loss of 13.8 per cent (276 cu. ft.) due to the reaction, leaving 1,724 cu. ft. of mixed gases, as follows:

$$\begin{aligned} 1724 \times 0.08 &= 138 \text{ cu. ft. CO}_2 \\ 1724 \times 0.08 &= 138 \text{ cu. ft. H}_2\text{O} \\ 1724 \times 0.34 &= 586 \text{ cu. ft. CO} \\ 1724 \times 0.50 &= 862 \text{ cu. ft. H}_2 \end{aligned}$$

The water in condensing leaves a net volume of permanent gases equal to 1724 - 138 = 1586 cu. ft. This permanent gas is composed of 8.7 per cent CO<sub>2</sub>, 37 per cent CO and 54.3 per cent H<sub>2</sub>. There would be also a deposit of 9.25 pounds of carbon. In other words, there are only 1586 - 138 = 1448 cu. ft. of the original H<sub>2</sub> and CO remaining.

Different temperature conditions would obviously give different results. A numerical problem of this nature shows how vitally equilibria conditions influence gas manufacture, and indicates the commercial importance of an understanding of such equilibria



conditions. Just as the equilibria conditions here are of importance, it can be shown that they are no less important when the reactions are between CO, H<sub>2</sub>, CO<sub>2</sub>, and H<sub>2</sub>O coming from the blue water gas on one hand, and H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, and tar vapors, etc., coming from the gas oil on the other hand.

The blue water gas reactions and equilibria have been investigated<sup>1</sup> and are well understood, so that we know what conditions are favorable and what are unfavorable; i. e., degree of temperature, quantity of steam, depth of fuel bed, etc.

#### MANUFACTURE OF STRAIGHT OIL GAS

The manufacture of an oil gas as carried out by the Pintsch or Blau Gas companies is an old process, but is not as well understood as the blue water gas equilibrium. Few experimental equilibria of the various components of oil gas have been worked out, as have been the CO<sub>2</sub>, CO, H<sub>2</sub>O and H<sub>2</sub> relations of blue water gas. Here, one at once faces the fact that in the oil cracking process, instead of the four gases of the blue water gas reaction, there are all the members of the methane, ethylene and acetylene series, as well as those hydrocarbons which constitute the tars produced in pyrogenetic decomposition.

Synthetic methane has been made from carbon and hydrogen,<sup>2</sup> where equilibrium exists when

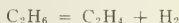
$$K = \frac{p_{\text{CH}_4}}{p_{\text{H}_2}^2}$$

Similarly, we may conclude that equilibrium exists between H<sub>2</sub> and all of the other hydrocarbons.

By combining the ethane and ethylene equations through the elimination of carbon, one gets C<sub>2</sub>H<sub>6</sub> = C<sub>2</sub>H<sub>4</sub> + H<sub>2</sub>, where equilibrium conditions prevail when

$$K = \frac{p_{\text{C}_2\text{H}_6} p_{\text{H}_2}}{p_{\text{C}_2\text{H}_4}}$$

For a practical illustration of the meaning of this expression, assume a volume of C<sub>2</sub>H<sub>6</sub> and heat it. Eliminating other reactions than the one between ethane and ethylene, consider the resultant relative quantities of H<sub>2</sub>, C<sub>2</sub>H<sub>6</sub> and C<sub>2</sub>H<sub>4</sub> at a temperature of 900° C., taking the value of *K* equal to 1.26



Let *X* = volume H<sub>2</sub>  
then *X* = volume C<sub>2</sub>H<sub>4</sub>  
 $\frac{1}{1+X}$  = volume C<sub>2</sub>H<sub>6</sub>  
∴  $\frac{1}{1+X}$  = total final volume

$$\frac{X}{1+X} = \text{partial pressure C}_2\text{H}_4 \quad \frac{1-X}{1+X} = \text{partial pressure C}_2\text{H}_6$$

$$\frac{X}{1+X} = \text{partial pressure H}_2$$

$$K = 1.26 = \frac{\left(\frac{X}{1+X}\right)\left(\frac{X}{1+X}\right)}{\left(\frac{1-X}{1+X}\right)} = \frac{X^2}{1-X^2}$$

Solving,  $X = 0.74$

$$\frac{0.74}{1.74} = 42.6 \text{ per cent C}_2\text{H}_4 \quad \frac{0.74}{1.74} = 42.6 \text{ per cent H}_2$$

$$\text{and } \frac{0.26}{1.74} = 14.8 \text{ per cent C}_2\text{H}_6$$

In dealing with any of these equilibria expressions, one must be careful to remember that no single equilibrium can be considered by itself. In the ethane-hydrogen-ethylene equilibrium at 900° C., for instance, there is a pronounced tendency for the ethane to go to ethylene; and in practice one should, therefore, expect a high ethylene yield, but by referring to the ethylene-benzene system one finds that at 900° C. there is an even greater tendency for the ethylene to be removed by polymerization to benzene. Assuming a volume of C<sub>2</sub>H<sub>4</sub> and bringing it to equilibrium at 900° C., observe the resultant relative quantities of C<sub>2</sub>H<sub>4</sub> and C<sub>6</sub>H<sub>6</sub>:



Under equilibrium conditions

*X* = volume C<sub>6</sub>H<sub>6</sub>

3*X* = volume H<sub>2</sub>

1 - 3*X* = volume C<sub>2</sub>H<sub>4</sub>

∴ 1 + *X* = total final volume

$$\frac{X}{1+X} = \text{partial pressure of C}_6\text{H}_6 \quad \frac{1-3X}{1+X} = \text{partial pressure C}_2\text{H}_4$$

$$\frac{3X}{1+X} = \text{partial pressure of H}_2$$

$$K = \frac{p_{\text{C}_6\text{H}_6} p_{\text{H}_2}^3}{p_{\text{C}_2\text{H}_4}^3} = 68 \times 10^8 = \frac{\left(\frac{X}{1+X}\right)\left(\frac{3X}{1+X}\right)^3}{\left(\frac{1-3X}{1+X}\right)^3} = \frac{27X^4}{(1+X)(1-3X)^4}$$

Solving,  $X = 0.33$

$$\frac{0.33}{1.33} = 24.8 \text{ per cent C}_6\text{H}_6 \quad \frac{0.99}{1.33} = 74.4 \text{ per cent H}_2$$

$$\text{and } \frac{0.01}{1.33} = 0.8 \text{ per cent C}_2\text{H}_4$$

Thus an experimental test, using the first equilibrium without a consideration of the second, would result in disappointment. Further, not only must the ethane-hydrogen-ethylene-benzene equilibrium be satisfied, but each of these constituents must, in turn, be in equilibrium with methane, acetylene, propane, naphthalene, etc. In short, there will be a grand symphony of equilibria between all components of the system.

Equilibrium expressions, such as the ones just given, are therefore of value when properly understood and used as a basis for experimental proof. First of all, the time element is very important to insure final equilibrium; and secondly, their mathematical derivations involve integration factors based on physical properties such as specific heat, vapor pressure, heat of reaction, etc., under conditions which have not been experimentally determined. Experimental demonstration based upon a few selected and isolated equilibria is almost certain to result in failure, due to overlooking other equally important equilibria which might modify or even reverse the direction of final reactions.

Sufficient experimental and commercial work has been done on the making of all oil gas under atmospheric conditions<sup>1</sup> to give empirical data indicating that as

<sup>1</sup> Bureau of Mines, Bulletin 7, 1911; Jüptner, Chem. Ztg., 1904, p. 902; K. Neuman, Stahl und Eisen, 1913, p. 394; O. Hahn, Z. physik. Chem., 44, 513-547; C. LeChâtelier and K. Neuman, Stahl und Eisen 1913, p. 1485; E. A. Allcut, Engineering, 1911, p. 601.

<sup>2</sup> Pring and Fairlie, Report of Eighth International Congress; Ipatiew, Jour. prakt. Chem., 1913, pp. 479-487; Pring and Fairlie, Jour. Chem. Soc., 1906 p. 1591; Ibid., 1911, p. 1796; Ibid., 1912, pp. 91-103; Bone and Coward, J. Chem. Soc., 1908, p. 1975. Proc. Chem. Soc., 1910, p. 146.

<sup>3</sup> Haber and co-workers, Jour. Gasb., 1896, pp. 377, 395, 435, 452; Hempel, Dissertation, Jour. Gasb., 1910, pp. 53, 77, 101, 137, 155.

the temperature goes above 800° C. the yield of hydrocarbons rapidly decreases; on the other hand, the hydrogen and carbon rapidly increase.

#### CARBURETED WATER GAS PROCESS

In the carbureted water gas practice as carried out to-day, there is a combination of the blue water gas and the oil gas process. Much is known about the blue gas; it is also known that this blue gas is carbureted by spraying in and cracking oil which furnishes the hydrocarbons and illuminants. There is little scientific information, however, regarding the interactions and equilibria which are reached when the two processes are combined. The formation of hydrocarbons and water from CO and H<sub>2</sub> or from CO<sub>2</sub> and H<sub>2</sub> is not theoretical speculation;<sup>1</sup> likewise the destruction of hydrocarbons with water to form CO and H<sub>2</sub> or CO<sub>2</sub> and H<sub>2</sub>, as carried out in the all oil gas process, is not theoretical speculation. Whichever course prevails depends entirely upon conditions. Consequently, one is justified in concluding that the present composition of carbureted water gas is not the result of additive processes. Instead there is a mixture of blue water gas and cracked oil gas passing through the

tendency of the American manufacturer to combine processes; it may appear that the attempt to do everything in a single vat rather than carry it out in stages is not the most economical method in the end.

#### EQUATIONS AND THEORETICAL EQUILIBRIA INVOLVED

The formation of methane from carbon monoxide and hydrogen, or from carbon dioxide and hydrogen is an exothermic reaction and consequently is favored by low temperatures, although at these low temperatures a greater amount of time is required for complete reaction. The reaction may be greatly stimulated by catalytic agents such as nickel and cobalt. In view of the fact that there is a decrease in volume, one should expect pressure to be favorable to hydrocarbon formation. Equilibrium exists between CO and H<sub>2</sub> or CO<sub>2</sub> and H<sub>2</sub> on the one side and CH<sub>4</sub> and H<sub>2</sub>O on the other.



with equilibrium established when

$$K = \frac{p_{\text{CO}} p_{\text{H}_2}^3}{p_{\text{CH}_4} p_{\text{H}_2\text{O}}} \text{ and } K' = \frac{p_{\text{CO}_2} p_{\text{H}_2}^4}{p_{\text{CH}_4} p_{\text{H}_2\text{O}}^2}$$

TABLE I—QUALITATIVE STUDY OF EQUILIBRIA

A	B	C
$\text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons \text{CO} + 3\text{H}_2$ $K = \frac{\text{CO} \times (\text{H}_2)^3}{\text{CH}_4 \times \text{H}_2\text{O}}$ $\text{C}_2\text{H}_4 + 2\text{H}_2\text{O} \rightleftharpoons 2\text{CO} + 4\text{H}_2$ $K = \frac{(\text{CO})^2 \times (\text{H}_2)^4}{\text{C}_2\text{H}_4 \times (\text{H}_2\text{O})^2}$ $\text{C}_2\text{H}_2 + 2\text{H}_2\text{O} \rightleftharpoons 2\text{CO} + 3\text{H}_2$ $K = \frac{(\text{CO})^2 \times (\text{H}_2)^3}{\text{C}_2\text{H}_2 \times (\text{H}_2\text{O})^2}$ FAVORABLE WHEN CO AND H <sub>2</sub> ARE LARGE AND H <sub>2</sub> O IS SMALL	$\text{CH}_4 + 2\text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + 4\text{H}_2$ $K = \frac{\text{CO}_2 \times (\text{H}_2)^4}{\text{CH}_4 \times (\text{H}_2\text{O})^2}$ $\text{C}_2\text{H}_4 + 4\text{H}_2\text{O} \rightleftharpoons 2\text{CO}_2 + 6\text{H}_2$ $K = \frac{(\text{CO}_2)^2 \times (\text{H}_2)^6}{\text{C}_2\text{H}_4 \times (\text{H}_2\text{O})^4}$ $\text{C}_2\text{H}_2 + 4\text{H}_2\text{O} \rightleftharpoons 2\text{CO}_2 + 5\text{H}_2$ $K = \frac{(\text{CO}_2)^2 \times (\text{H}_2)^5}{\text{C}_2\text{H}_2 \times (\text{H}_2\text{O})^4}$ FAVORABLE WHEN CO <sub>2</sub> AND H <sub>2</sub> ARE LARGE AND H <sub>2</sub> O IS SMALL	$\text{CH}_4 + \text{CO}_2 \rightleftharpoons 2\text{CO} + 2\text{H}_2$ $K = \frac{(\text{CO})^2 \times (\text{H}_2)^2}{\text{CH}_4 \times \text{CO}_2}$ $\text{C}_2\text{H}_4 + 2\text{CO}_2 \rightleftharpoons 4\text{CO} + 2\text{H}_2$ $K = \frac{(\text{CO})^4 \times (\text{H}_2)^2}{\text{C}_2\text{H}_4 \times (\text{CO}_2)^2}$ $\text{CH}_2 + 2\text{CO}_2 \rightleftharpoons 4\text{CO} + \text{H}_2$ $K = \frac{(\text{CO})^4 \times \text{H}_2}{\text{C}_2\text{H}_2 \times (\text{CO}_2)^2}$ FAVORABLE WHEN CO AND H <sub>2</sub> ARE LARGE AND CO <sub>2</sub> IS SMALL

carbureter and superheater which constitute a single unbalanced system of gases; naturally, there is a tendency to establish equilibrium between the constituents just as surely as there is a tendency to establish an equilibrium between the constituents of either the blue gas or the all oil gas when made individually. This equilibrium at the usual temperature of the superheater has fortunately favored the formation, or at least the preservation, of hydrocarbons. This fact, however, does not prove that the process is working under conditions of, or approaching, maximum efficiency. Nor does it prove that the present method of carbureting water gas is the most economical from the side of the quantity of gas oil consumed.

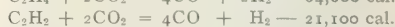
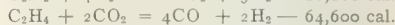
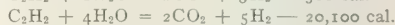
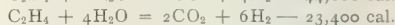
Many questions arise at this point. It might be possible to alter conditions in such a way as to solve or assist in solving the naphthalene and carbon problems of the gas manufacturer. It might still further be worth while to question the soundness of the natural

Combining the two equations with elimination of H<sub>2</sub>O,



$$K'' = \frac{p_{\text{CO}}^2 p_{\text{H}_2}^2}{p_{\text{CH}_4} p_{\text{CO}_2}}$$

In like manner the equilibria between CO, CO<sub>2</sub>, and H<sub>2</sub>O, on the one side, and C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub> and H<sub>2</sub>O on the other, are considered below:



With these there is sufficient data to determine in a qualitative way the concentration conditions favorable to the methane, ethylene and acetylene desired in the resultant gas (see Table I).

The original complex state of affairs is thus partially clarified. One sees that conditions favorable to the formation of hydrocarbons, or at least unfavorable to the decomposition of hydrocarbons, exist when in

A, B and C there is an excess of H<sub>2</sub>,

A and C, there is an excess of CO,

A and B, there is a minimum of water vapor,

B, there is an excess of CO<sub>2</sub>,

C, there is a minimum of CO<sub>2</sub>.

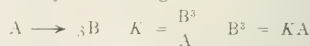
<sup>1</sup> Mayer, Henseling and Altmayer, *J. Gasb.*, **1909**, pp. 166, 194, 238, 326; P. Sabatier, *Chem. Ztg.*, **1913**, p. 148; P. Sabatier, Fr. Patent 355,325, **1905**; *Ibid.*, 355,900, **1905**; *Ibid.*, 361,616; *Ibid.*, 400,656; Eng. Patent 14,971, **1908**; *Ibid.*, 27,043. L. Vignon, Fr. Patent 416,009, **1909**; *Comp. rend.*, **1913**, pp. 131-134; Gautier, *Ibid.*, **1910**, p. 1565; Ellsworth and Williamson, Eng. Patent 12,461, **1902**; Bedford and Williams, Eng. Patents 17,017, 22,219, **1909**; H. J. Coleman, *Jour. Gas Lighting*, **1908**, p. 683; E. Erdman, *Jour. Gasb.*, **1911**, pp. 737-743; E. Oriow, *Jour. Russ. Phys. Chem.*, **1908**, p. 1588; P. Jockum, *Jour. Gasb.*, **1914**, pp. 73, 103, 124, 149; T. Holgate, *Gas World*, **1914**, p. 90; German Patents 183,412, 190,201, 191,026, 237,499, 226,942, 177,703, 174,343 and 250,909.





For numerical illustration, assume the value of  $K$  to be equal to 1 (any other value serving equally well). From this, one finds for partial pressures, when  $A = 100$ ,  $B = 10$  or when  $A = 0.01$ ,  $B = 0.1$ . In the first case the partial pressure of  $A$  is ten times as great as that of  $B$ ; in the second case the partial

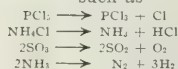
The general relationship of  $B$  to  $A$  changes only in degree the greater the change in the number of volumes, as can be seen by considering the curve for



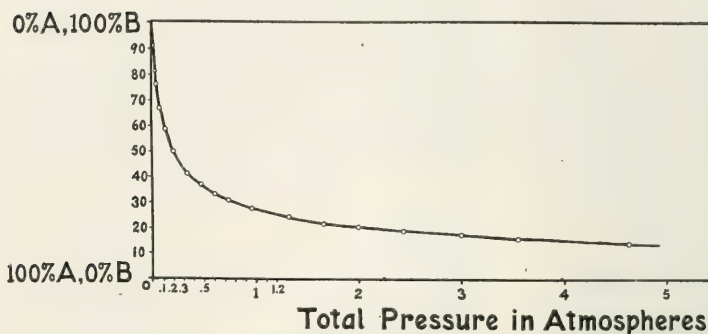
From the curves shown, one can readily see that the effect of reducing pressure from one atmosphere to two-thirds of an atmosphere gives an advantage which is of little practical consequence when compared with the advantage gained by the same reductions when nearer the absolute zero of pressure. One-thirtieth of an atmosphere added to one-thirtieth atmosphere pressure doubles the total pressure on a system just as effectively as an increase from 100 to 200 atmospheres.

#### EFFECT OF CONCENTRATION IN GASEOUS REACTIONS

The addition of an end product in any decomposition or dissociation process, such as



checks the decomposition or dissociation. In other words, less  $\text{PCl}_5$  will dissociate in an atmosphere of chlorine than in an atmosphere of nitrogen or air. Ammonium chloride when heated in an atmosphere of



CURVE I—REACTION ISOTHERM

pressure of  $A$  is only one-tenth as large as the partial pressure of  $B$ . In other words, by simply changing the total pressure on the system and keeping all other conditions constant, the ratio of  $A$  to  $B$  for the pressures shown has been divided by 100. By taking the first differential of the relationship, and equating it to 0,

$$\begin{aligned} K &= \frac{B^2}{A} & A &= \frac{B^2}{K} \\ dA &= \frac{2B}{K} dB = 0 & \therefore B &= 0 \\ dB &= K \end{aligned}$$

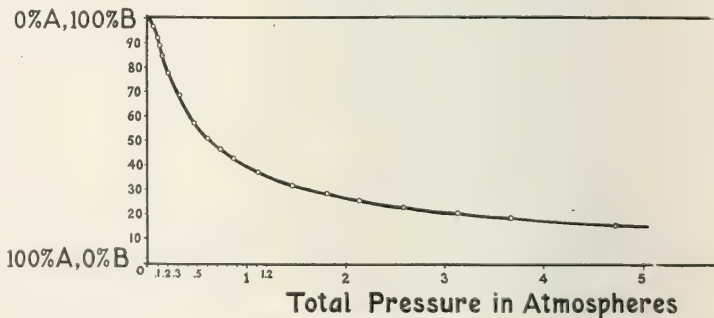
one sees there is a maximum or minimum in the ratio of  $A$  to  $B$  as zero pressure is approached. By taking the second differential

$$\frac{d^2A}{dB^2} = + \frac{2}{K}$$

one finds the sign to be positive, indicating that the partial pressure of  $A$  as compared with the partial pressure of  $B$  approaches a minimum as the pressure approaches the absolute zero; or conversely there would be a maximum relative yield of  $B$  the closer

one approached zero pressure absolute. The rate of change can best be seen by determining points for the parabola,  $B^2 = KA$ , and plotting the resulting curve.<sup>1</sup>

<sup>1</sup> Since most of the values of  $K$  encountered in the practical study of the problem were represented by decimals, Curves I and II were plotted on the basis of  $K = 0.1$ .



CURVE II—REACTION ISOTHERM

ammonia will not dissociate to the same extent as in a vacuum or in an atmosphere containing neither ammonia nor hydrochloric acid gas. Likewise it would be expected that ethylene would not decompose to the same degree when subjected to a high temperature in

the presence of hydrogen as when subjected to the same temperature in an atmosphere of nitrogen. Further, if the ethylene were subjected to the same high temperature in the presence of both hydrogen and methane, these two constituents in the ethylene-methane-hydrogen equilibrium could be in excess; as a result, less of the ethylene should be decomposed in the formation of methane and hydrogen. Broadly speaking, to crack petroleum in an atmosphere containing all the hydrocarbon gases with the exception of ethylene, one would expect all the fixed gas coming from the petroleum to be ethylene, at least until the ethylene content of the system is sufficient to conform to the equilibrium conditions. The consideration of these principles seems to question the necessity of using valuable gas oil in continually generating new end products, such as tar and hydrogen; if they could be artificially supplied the equilibrium conditions would be satisfied without producing new decomposition and polymerization end products.

#### COMBINED INFLUENCE OF PRESSURE AND CONCENTRATION ON GASEOUS REACTIONS

Theoretical consideration of the effect of pressure on gaseous reactions indicates that an increased yield of gaseous hydrocarbons will be obtained as the total pressure on the system approaches zero; also an increased yield of illuminants will be obtained by cracking the oil in an atmosphere of end products such as hydrogen and methane. On combination the logical conclusion is that one should obtain the maximum yield of illuminants by cracking the petroleum at low pressures and in an atmosphere of end products. Upon first consideration one might reasonably question the idea of adding hydrogen or methane to a vacuum, but this investigation deals with relative partial pressures, regardless of whether the total pressure equals fifty atmospheres or one-fiftieth of one atmosphere absolute.

#### INFLUENCE OF CATALYSTS ON GASEOUS REACTIONS

Catalytic agents such as platinum, palladium, cobalt and nickel do not, in any way, influence final conditions of equilibrium; they merely hasten the rate at which the system reaches its final equilibrium. Whereas ethylene and hydrogen do not combine to an appreciable degree when heated to 100° C. in the absence of a catalyzer, the same mixture passed over colloidal palladium heated to 100° C. unites to form a considerable percentage of ethane. Likewise CO and H<sub>2</sub> or CO<sub>2</sub> and H<sub>2</sub> can be in intimate contact at 200° to 300° without appreciable reaction in the formation of methane, but when the same proportions are brought together in the presence of a catalytic agent such as nickel or cobalt there is a very large yield of methane and water.<sup>1</sup> Vignon<sup>2</sup> finds that lime has much the same effect on the combination of CO and H<sub>2</sub>.

#### THE VAN'T HOFF DIFFERENTIAL EQUATION SHOWING THE RELATION OF K TO K'

To all students of physical chemistry the proposi-

<sup>1</sup> Mayer, Henseling and Altmayer, *Jour. f. Gasb.*, **1909**, pp. 1106, 194; Jockum, *Ibid.*, **1914**, pp. 73, 103, 124, 149; Orlov, *Jour. Russ. Phys. Chem.*, **1908**, p. 1588.

<sup>2</sup> Vignon, *L., Compt. rend.*, **1913**, pp. 131-134.

tion of Berthelot and Thomson that "every chemical change gives rise to the production of those substances which occasion the greatest development of heat" is familiar. Were this true, it would be easy to predict which of two given reactions would take place at a given temperature. Chemists today recognize the fallacy of the statement because in all chemical reactions one deals with the additional so-called "latent energy." Berthelot's principle disregards this molecular energy, and assumes the free energy, termed maximum work, to be equal to the total energy change. Nernst maintains that this is true only at the absolute zero, *i. e.*, the entropy of liquids and solids at absolute zero temperature equals zero.

The van't Hoff equation showing the relation between *K* and *K'* is expressed by

$$\frac{d}{dT} (\log e K_p) = \frac{-q_p}{RT^2} \text{ or } d (\log e K_p) = \frac{-q_p}{R} \frac{dT}{T^2}$$

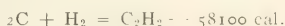
Upon integration this becomes

$$\log e K_p = \frac{q_p}{RT} + \text{constant}$$

Were it a simple matter to determine the value of this constant of integration, as well as the value of *q* at the different temperatures (in other words integrate the expression to absolute units) this would constitute a mathematical expression for what some consider a third law of thermodynamics. As yet there is no such accepted integration, and the best solution is to use approximate expressions, remembering at all times that the expressions are approximate, and making intelligent use of them as such. It is possible to avoid the constant of integration, however, by integrating between limits *p'* and *p* to

$$\log e K_{p'} - \log e K_p = \frac{q_p}{R} \left( \frac{1}{T'} - \frac{1}{T} \right)$$

This integrated expression is extremely important in determining the value of *K'* for any desired temperature after the value of *K* for any other temperature has been experimentally determined. It is also of value in showing relationships between *K* and *K'* for two different temperatures, where neither has been determined, but in this case it expresses relationships and not direct values. For instance, assume that one wished to find the relationship between *K* and *K'* for the reaction



at the temperatures 600° and 900° C.

$$\log e K_{p'} - \log e K_p = \frac{58100}{2} \left( \frac{1}{1173} - \frac{1}{873} \right) = 8.49$$

$$\log e \frac{K_{p'}}{K_p} = 8.49 \text{ or, } \log_{10} \frac{K_{p'}}{K_p} = 3.60$$

whence

$$K_{600} = \frac{K_{900}}{4900}$$

#### THE NERNST APPROXIMATION FORMULA FOR K

Even though correct, *K* is a value based on the assumption that sufficient time elapses to allow the system to reach complete equilibrium. When dealing

with hydrocarbons at different temperatures, this must not be overlooked. In fact the time element is of such primary moment that numerically correct values for  $K$  would be of little more practical use in gas manufacture than approximate values. In the case of reacting gases one does not have the speed conditions that ordinarily exist in solutions. On the other hand, gases brought together at sufficiently high temperatures do reach equilibrium practically instantly. It is important to bring out these limitations despite the value of approximate quantitative expressions such as the Nernst formula; they are of immense value in predicting the tendency of a reaction. In this paper the expression is merely used; its derivation with comments can be found in the seventh German edition of Nernst's "Theoretical Chemistry," Jellinek's "Physikalische Chemie der Gasreaktionen," or Sackur's "Thermochemie und Thermodynamik."

$$\log K = \frac{q}{4.571T} + \Sigma v \cdot 1.75 \log T + \Sigma vC$$

where  $q$  is the heat developed at ordinary temperatures and under constant pressure, as taken from thermochemical tables;  $\Sigma v$  represents the volume changes, and  $\Sigma vC$  represents a summation of constants. These constants are given as follows:

H <sub>2</sub>	1.6	C <sub>2</sub> H <sub>6</sub>	2.6	C <sub>2</sub> H <sub>2</sub>	3.2	CO	3.5	H <sub>2</sub> O	3.6
CH <sub>4</sub>	2.5	C <sub>2</sub> H <sub>4</sub>	2.8	C <sub>2</sub> H <sub>6</sub>	3.0	CO <sub>2</sub>	3.2	O <sub>2</sub>	2.8

To use Nernst's words, the equation gives a "fairly accurate" idea of the state of equilibrium in a system.

The approximation is applied in this fashion:



$$\log K_{800} = \frac{+18900}{4.571 \times 873} - 1.75 \log 873 - 0.7 = -1.11 = 2.89(a)$$

$$\log K_{780} = \frac{+18900}{4.571 \times 1023} - 1.75 \log 1023 - 0.7 = -1.93 = 2.07$$

$$\log K_{800} = \frac{+18900}{4.571 \times 1173} - 1.75 \log 1173 - 0.7 = -2.55 = 3.45$$

whence,

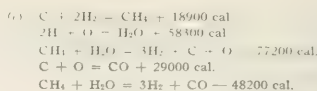
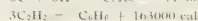
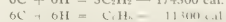
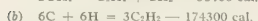
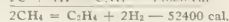
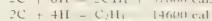
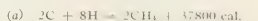
$$K_{800} = 0.077 \quad K_{780} = 0.012 \quad K_{800} = 0.003$$

(a) Negative logarithms must be converted into logarithms with positive mantissa.

In similar manner, the values of  $K$ ,  $K'$ , and  $K''$  for Equations 1, 2, 3, 4, 5, 6, 7, 13, 16, 17, 18, and 22 in Table II have been calculated. In those reactions involving CO and CO<sub>2</sub>, as 19, 23, and 26, use has been made of the approximation formulas for the same as worked out by Mayer and co-workers,<sup>1</sup> but substituting the values of  $q$  shown in the table.

#### CALCULATION OF HEATS OF REACTIONS FOR DIFFERENT EQUILIBRIA

The heat absorbed or emitted in a given reaction was determined by means of the ordinary thermochemical methods of addition and subtraction, as in the following typical examples:



It is likewise possible to combine the values of  $K$  for one reaction with  $K'$  for a second reaction in order to determine  $K''$  for the resultant reaction.

$$C + 2H_2 = CH_4 \quad K = \frac{p_{CH_4}}{p_{H_2}^2}$$

$$2C + H_2 = C_2H_2 \quad K' = \frac{p_{C_2H_2}}{p_{H_2}}$$

Dividing the square of the methane equilibrium by the acetylene equilibrium, one gets

$$K'' = \frac{(K')^2}{(K)^2} = \frac{p_{C_2H_2}^2 p_{H_2}^2}{p_{CH_4}^2} = \frac{p_{C_2H_2}^2 p_{H_2}^2}{p_{CH_4}^2}$$

This operation can be represented by the equation



In this work the values of  $K$  and  $K'$  have been combined in the manner just shown in order to determine values for equations 8, 9, 10, 11, 12, and 14. The Nernst approximation formula could be applied directly to each of these equations with the same results. All reactions indicated in Table II may go in either direction. Attention is again called to the fact that the reactions given must be used with a consideration of all factors involved; no equation by itself represents a complete system. All the gases mentioned, together with many others, are tending to reach equilibrium with one another. Tar compounds were not listed. Benzene, C<sub>6</sub>H<sub>6</sub>, has been used as typical of all tar formations. In technical practice one gets benzene and other tar compounds from methane hydrocarbons; from experimental evidence, it is known that from ethylene<sup>1</sup> or acetylene<sup>2</sup> the same results are reached. Throughout the literature one finds questions as to whether methane goes to acetylene, or acetylene to methane, ethane to ethylene, ethylene to ethane, etc. Considered in the light of this study it appears that regardless of which hydrocarbon is used initially there is a pronounced tendency for the system to reach a common equilibrium dependent upon the existing temperature. With hydrocarbons the result seems to depend more upon conditions of temperature, pressure and concentration than upon the initial hydrocarbons. In other words, with proper conditions of temperature, pressure and concentration, and with sufficient time for complete reaction, the final equilibrium will be that of the mentioned hydrocarbons. and their reaction products, regardless of whether decane, hexane, ethane, methane, ethylene or acetylene,<sup>3</sup> singly or in mixtures, are used in the beginning.

Table II furnishes the basis for the experimental work of this research. Its interpretation serves as a guide in determining the direction of experiments.

<sup>1</sup> Ipatiew, *Ber.*, **1911**, p. 2978; Ipatiew and Rontala, *Ibid.*, **1913**, p. 1748

<sup>2</sup> R. Meyer, *Ibid.*, **1912**, p. 1609; Meyer and Tanzen, *Ibid.*, **1913**, p. 3183

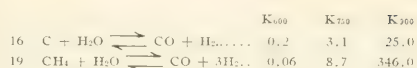
<sup>3</sup> W. A. Bone, *Jour. T. Gasch.*, **1908**, p. 803; D. T. Day, *Am. Chem. Jour.*, **1886**, p. 153; V. Lewes, *Proc. Roy. Soc.*, **1894**, p. 90; Worstell and Burwell, *Am. Chem. Jour.*, **1897**, p. 815; Bone and Coward, *Jour. Chem. Soc.*, **1908**, p. 1197; Sabatier and Senderens, *Compt. rend.*, **130**, 1559; C. Paal, *Chem. Ztg.*, **1912**, p. 60; Ipatiew, *Ber.*, **44**, 2987.

<sup>1</sup> Mayer, Henseling and Altmayer, *Jour. Gasch.*, **1909**, pp. 166, 194, 238



Taking Equation 9 as typical, where  $K_{600} = 0.0000001$  and  $K_{900} = 0.0004$ , it seems advisable to exceed  $900^\circ$  C. in temperature. However, referring to  $K_{600} = 0.077$  and  $K_{900} = 0.003$  for Equation 3, it is evident that the rate at which methane would decompose to carbon and hydrogen, in accordance with Equation 3, might easily be sufficient to offset all  $C_2H_4$  formation, in accordance with Equation 9.

Considering Equations 16 and 19, two of the most vital in present carbureted water gas manufacture, one finds



and that a temperature of  $900^\circ$  C. is favorable to the CO and  $H_2$  formation of 16, but unfavorable to the methane preservation in Equation 19. On the other hand, a temperature of  $600^\circ$  C. is unfavorable to preservation of CO and  $H_2$  in Equation 16 but is more favorable than  $900^\circ$  to hydrocarbon formation or preservation. Also it is more favorable to formation of  $CO_2$  as shown by Equation 17. These temperature effects can be

TABLE II. QUANTITATIVE STUDY OF EQUILIBRIA

No.	REACTIONS	HEATS OF REACTION	VOLUME CHANGES	(Formulas refer to partial pressures)	APPROXIMATE		
					$K_{600}$	$K_{750}$	$K_{900}$
1.	$C + O_2 \rightleftharpoons CO_2$	+97650	1 to 1	$K = \frac{CO_2}{O_2}$	$6.9 \times 10^{14}$	$1.9 \times 10^{14}$	$1 \times 10^{18}$
2.	$CO_2 + C \rightleftharpoons 2CO$	-39650	1 to 2	$K = \frac{(CO)^2}{CO_2}$	0.1	3.9	59.0
3.	$C + 2H_2 \rightleftharpoons CH_4$	+18900	2 to 1	$K = \frac{CH_4}{(H_2)^2}$	0.077	0.012	0.003
4.	$2C + 3H_2 \rightleftharpoons C_2H_6$	+23300	3 to 1	$K = \frac{C_2H_6}{(H_2)^3}$	$2.2 \times 10^{-7}$	$1.7 \times 10^{-8}$	$2.5 \times 10^{-9}$
5.	$2C + 2H_2 \rightleftharpoons C_2H_4$	-14600	2 to 1	$K = \frac{C_2H_4}{(H_2)^2}$	$6.0 \times 10^{-10}$	$1.6 \times 10^{-9}$	$3.2 \times 10^{-9}$
6.	$2C + H_2 \rightleftharpoons C_2H_2$	58100	1 to 1	$K = \frac{C_2H_2}{H_2}$	$1.1 \times 10^{-11}$	$1.5 \times 10^{-11}$	$5.7 \times 10^{-10}$
7.	$6C + 3H_2 \rightleftharpoons C_3H_6$	-11300	3 to 1	$K = \frac{C_3H_6}{(H_2)^3}$	$1.2 \times 10^{-15}$	$1.7 \times 10^{-15}$	$2.2 \times 10^{-14}$
8.	$C_2H_6 \rightleftharpoons C_2H_4 + H_2$	-37900	1 to 2	$K = \frac{C_2H_4 \times H_2}{C_2H_6}$	0.0027	0.094	1.28
9.	$2CH_4 \rightleftharpoons C_2H_6 + 2H_2$	-52400	2 to 3	$K = \frac{C_2H_6 \times (H_2)^2}{(CH_4)^2}$	0.0000001	0.00001	0.0004
10.	$2CH_4 \rightleftharpoons C_2H_2 + 3H_2$	-95900	2 to 4	$K = \frac{C_2H_2 \times (H_2)^3}{(CH_4)^2}$	$1.86 \times 10^{-11}$	0.0000001	0.00006
11.	$C_2H_6 \rightleftharpoons C_2H_4 + H_2$	-43500	1 to 2	$K = \frac{C_2H_4 \times H_2}{C_2H_6}$	0.00018	0.0093	0.178
12.	$C_2H_6 \rightleftharpoons C_2H_2 + 2H_2$	-81400	1 to 3	$K = \frac{C_2H_2 \times (H_2)^2}{C_2H_6}$	0.0000005	0.00089	0.228
13.	$C_2H_6 \rightleftharpoons 2C_2H_2$	-31800	1 to 2	$K = \frac{(C_2H_2)^2}{C_2H_6}$	1.41	31.6	258.0
14.	$3C_2H_2 \rightleftharpoons C_6H_6$	+163000	3 to 1	$K = \frac{C_6H_6}{(C_2H_2)^3}$	$9 \times 10^{12}$	$5 \times 10^{17}$	$1.2 \times 10^{12}$
15.	$3C_2H_4 \rightleftharpoons C_6H_6 + 3H_2$	+32500	3 to 4	$K = \frac{C_6H_6 \times (H_2)^3}{(C_2H_4)^3}$	$5.5 \times 10^{12}$	$4.1 \times 10^{11}$	$6.7 \times 10^{10}$
16.	$C + H_2O \rightleftharpoons CO + H_2$	-29300	1 to 2	$K = \frac{CO \times H_2}{H_2O}$	0.2	3.1	25
17.	$C + 2H_2O \rightleftharpoons CO_2 + 2H_2$	-19000	2 to 3	$K = \frac{CO_2 \times (H_2)^2}{(H_2O)^2}$	0.4	2.5	11
18.	$H_2O + CO \rightleftharpoons CO_2 + H_2$	+10350	2 to 2	$K = \frac{CO_2 \times H_2}{H_2O \times CO}$	1.95	0.81	0.42
19.	$CH_4 + H_2O \rightleftharpoons CO + 3H_2$	-48200	2 to 4	$K = \frac{CO \times H_2^3}{CH_4 \times H_2O}$	0.06	8.7	346.0
20.	$C_2H_6 + 2H_2O \rightleftharpoons 2CO + 4H_2$	-44000	3 to 6	$K = \frac{(CO)^2 \times (H_2)^4}{C_2H_6 \times (H_2O)^2}$			
21.	$C_2H_2 + 2H_2O \rightleftharpoons 2CO + 3H_2$	-500	3 to 5	$K = \frac{(CO)^2 \times (H_2)^3}{C_2H_2 \times (H_2O)^2}$			
22.	$C_2H_4 + 6H_2O \rightleftharpoons 6CO + 9H_2$	-164500	1 to 15	$K = \frac{(CO)^6 \times (H_2)^9}{C_2H_4 \times (H_2O)^6}$	$1.2 \times 10^{-7}$	0.49	48000
23.	$CH_4 + 2H_2O \rightleftharpoons CO_2 + 4H_2$	-37900	3 to 5	$K = \frac{CO_2 \times (H_2)^4}{CH_4 \times (H_2O)^2}$	0.3	16	280
24.	$C_2H_6 + 4H_2O \rightleftharpoons 2CO_2 + 6H_2$	+23400	5 to 8	$K = \frac{C_2H_6 \times (H_2O)^4}{(CO_2)^2 \times (H_2)^6}$			
25.	$C_2H_2 + 4H_2O \rightleftharpoons 2CO_2 + 5H_2$	+20100	5 to 7	$K = \frac{C_2H_2 \times (H_2O)^4}{(CO_2)^2 \times (H_2)^5}$			
26.	$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2$	-58500	2 to 4	$K = \frac{CH_4 \times CO_2}{(CO)^2 \times (H_2)^2}$	0.017	5	354
27.	$C_2H_6 + 2CO_2 \rightleftharpoons 4CO + 2H_2$	-64600	3 to 6	$K = \frac{C_2H_6 \times (CO_2)^2}{(CO)^4 \times (H_2)^2}$			
28.	$C_2H_2 + 2CO_2 \rightleftharpoons 4CO + H_2$	-31100	3 to 5	$K = \frac{C_2H_2 \times (CO_2)^2}{(CO)^4 \times H_2}$			

more clearly understood by reference to the first numerical problem cited, and to the theoretical mixtures given for Equation 19 at temperatures of 600° and 900° C. It appears impossible to find a temperature favorable to both when the two reactions are simultaneously carried out. In order to preserve the hydrocarbons it becomes necessary to form H<sub>2</sub>O, CO<sub>2</sub> and deposit carbon; or in order to avoid forming water vapor, CO<sub>2</sub> and deposit carbon, it becomes necessary to destroy hydrocarbons. The two cannot be reconciled.

#### SUMMARY

On theoretical grounds, therefore, it appears:

I—Possible to so create conditions that the oil cracking process can be carried out at a higher temperature than is now used in oil gas processes, and thereby greatly increase the yield of valuable hydrocarbons.

II—Possible to "crack" oil without depositing carbon, and without the formation of water vapor and CO<sub>2</sub>.

III—Possible to partially control the quantity and composition of "tar" produced in gas manufacture.

IV—Impossible to preserve hydrocarbons and at the same time avoid CO<sub>2</sub>, water vapor, and deposited carbon, when oil is "cracked" as in the present carbureted water gas process.

Interpretation of Table II and the results which could be expected in gas reactions, involving the constituents shown, could be expanded indefinitely. That these theoretical considerations are of more than academic interest will be brought out in subsequent papers.

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### A METHOD FOR THE DETERMINATION OF MAGNESIUM IN CALCIUM SALTS<sup>1</sup>

By J. C. HOSTETTER

In the course of the preparation of some calcium silicates for thermal study, certain samples of calcium carbonate were tested to determine their suitability as sources of lime. Analyses of these samples showed that, of the non-volatile impurities determined by the makers, the amounts reported by them were substantially correct for all elements<sup>2</sup> except magnesium. This element was found to be present to the extent of several tenths of a per cent as oxide, even though the salts analyzed were of the very highest grades obtainable, and the makers' analyses had shown but a "trace," or, at most, 0.005 per cent MgO. A discrepancy of this large order could hardly be passed over without investigation, even though the problem thus presented was but a mere side issue. The writer's results on these samples had been obtained by the calcium sulfate separation, but, since the laboratory manipulation of this method was too involved for routine testing when large samples were taken, a method was developed by means of which very small amounts

of magnesium could be determined in the presence of much calcium, and which involved only the simplest laboratory manipulation. After this method had been developed, a number of calcium salts, from both domestic and foreign makers, were tested to determine their suitability for the particular problem in hand, but the surprisingly large quantities of magnesium found to be present were the source of much disappointment. In a few cases, the makers' results were of the same order of magnitude as those obtained by the new method, but usually the magnesia actually present was from fifty to even several hundred times greater than that reported by the maker. The probable source of the observed differences will appear in what follows.

Most of the methods employed for the determination of magnesium in the presence of calcium involve a removal of the latter by precipitation and a subsequent estimation of the former in the filtrate. In general, when testing for minute amounts of impurity, the procedure of first removing the main element by precipitation should never be followed. In some cases it can be justified, but these are rare and they can be determined only by direct test; in the greater number of cases the precipitating salt carries with it a large portion, if not all, of the impurity, and hence the amount of the latter subsequently found is much less than that actually present. Many methods of separation which are excellent when applied to tests in which the elements to be separated are present in nearly equal amounts fail utterly when the one element is present to the extent of a thousand times that of the other. This latter condition is the main one involved in the problem here studied, and failure to recognize this is the general reason why chemical manufacturers have often failed to find all of the magnesium present in their calcium salts. The specific manner in which loss of magnesium may occur in the ordinary methods of separating calcium and magnesium will appear in the discussion which follows.

**REMOVAL OF CALCIUM AS OXALATE**—The extensive investigation of Richards, McClaffrey and Bisbee<sup>1</sup> on the occlusion of magnesium by calcium oxalate has shown that when the latter is precipitated in the presence of magnesium under certain conditions, the resulting calcium oxide may carry as much as 16.4 per cent MgO; under the usual conditions for this precipitation, the occlusion may still amount to about 1 per cent. Only with careful attention to the details of the method proposed by them can a satisfactory separation of calcium from magnesium be made with one precipitation of the calcium oxalate.

Ordinarily, in exact analysis, two precipitations of the oxalate are deemed necessary for a good separation, and when the elements are present in nearly the same amount, this is justified. When large amounts of calcium and mere traces of magnesium are present, however, two precipitations, or even more, will not separate these two elements quantitatively.

In view of the convincing character of the work

<sup>1</sup> Read at the Rochester Meeting of the American Chemical Society, September 11, 1913.

<sup>2</sup> With the possible exception of sodium, for which the makers' "trace" was found to be 0.02 per cent Na<sub>2</sub>O

<sup>1</sup> *Z. anorg. Chemie*, **28** (1901), 71; *Proc. Am. Acad. Arts Sci.*, **36** (1901), 375

cited above, it is indeed surprising that texts on the subject of reagent testing should continue to prescribe the determination of magnesium in a solution from which calcium has been removed as oxalate, when calcium salts are to be tested for this impurity. As carried out by Krauch,<sup>1</sup> and by Krauch-Merck,<sup>2</sup> the calcium of 1 gram of the salt is precipitated as oxalate and the salt is considered satisfactory if sodium phosphate solution gives no precipitate in the filtrate on standing twelve hours.

**REMOVAL OF CALCIUM AS SULFATE**—This separation, as outlined by Classen,<sup>3</sup> is comparatively free from the errors inherent in the oxalate and carbonate precipitations. That calcium sulfate precipitated in the presence of magnesium carries a negligible amount of magnesia (occluded or otherwise) is shown by the following experiment: The calcium of 5 grams of a pure calcium chloride in alcoholic solution was precipitated with sulfuric acid in the presence of 250 mg. MgO (added as chloride). The calcium sulfate was filtered off and washed with 50 per cent alcohol in the prescribed manner. After drying, the magnesia was determined in this calcium sulfate by the new method to be described shortly, and found to be but 0.005 per cent.<sup>4</sup> In many cases the magnesia thus lost would be insignificant, but this loss could not be tolerated in the analysis of the purest calcium salts.

Though this method of removing calcium is fairly satisfactory in regard to the amount of magnesia occluded, it has the disadvantage that when large amounts of calcium are to be removed, the laboratory manipulation becomes difficult. This is due to the bulky nature of the precipitated calcium sulfate, the many tedious washings of the precipitate which are required, and the evaporation to dryness of several liters of alcoholic solution. Accordingly, we have discontinued the use of this method except as an occasional check.

The discrepancy observed between the makers' magnesia determinations and the writer's results by the calcium sulfate separation can be completely accounted for on the reasonable assumption that the makers follow the oxalate separation as given in the standard texts on reagent testing. Direct evidence on this point is generally lacking, but in the case of one maker at least, the labels specify that the salt has been tested according to Krauch.<sup>5</sup> In the absence of specific information on this subject from the other makers,<sup>6</sup> we can only assume that their results were also secured with the calcium oxalate separation on a comparatively small sample.

**REMOVAL OF CALCIUM AS CARBONATE**—It is well known that the separation of calcium as carbonate involves the same source of error as the oxalate separa-

tion—some magnesium is occluded by the calcium carbonate. The extent of this occlusion is indicated by the amount of MgO remaining in calcium carbonates of the highest grade—about 0.08 per cent.<sup>1</sup>

**THE METHOD OF HILDEBRAND AND HARNED**—This excellent method for the determination of magnesium in the presence of calcium (and other metals) is a precipitation of the magnesium as hydroxide, the precipitant being sodium hydroxide and the changes in hydrogen ion concentration being followed by means of the hydrogen electrode.<sup>2</sup> Since the uncertainty in the end point, as given by them, may amount to as much as 4 mg. MgO, it is evident that this method could be used in connection with the present problem only in the case of highly impure calcium salts.

#### THE PROPOSED METHOD

The essential feature of the method that follows is the *concentrating* of the magnesium from a large sample of the salt being tested into a precipitate containing but a small proportion of the calcium. After this has been accomplished the ordinary methods may be used to separate these elements with satisfactory results, since the ratio CaO : MgO is no longer 1,000 or 10,000 : 1, but has been reduced to 10 or 100 : 1. This concentrating is effected by precipitating the magnesium as hydroxide by adding either calcium oxide (made, in many cases, by ignition of the salt itself) or a solution of sodium hydroxide in slight excess over that necessary to precipitate the magnesium.<sup>3</sup> The details of the method follow.

Ten grams of the calcium salt are brought into solution in water, and the volume made up to 100 cc. If acid is used to bring the salt into solution, the excess is neutralized with sodium hydroxide, *after* the expulsion of CO<sub>2</sub>, SO<sub>2</sub>, etc., by boiling. The calcium oxide made from 0.3 to 0.5 gram<sup>4</sup> calcium carbonate by ignition is now added and the solution heated to boiling; the precipitate is filtered off but not washed. The precipitate is dissolved in dilute hydrochloric acid and the calcium removed by two precipitations with ammonium oxalate. The filtrates from these two precipitates are combined and the magnesium in this combined filtrate is determined by precipitation as ammonium magnesium phosphate with microcosmic salt. This precipitation is easily brought about by shaking in a stoppered flask. After standing several hours, the precipitate is filtered off, washed free from phosphoric acid with 10 per cent ammonia, and finally ignited to magnesium pyrophosphate which is weighed.

#### FACTORS AFFECTING THIS METHOD

**I. SOLUBILITY OF CALCIUM HYDROXIDE IN SOLUTIONS OF CALCIUM CHLORIDE**—A knowledge of the solubility of calcium hydroxide in 10 per cent calcium chloride solution is necessary in order to determine the amount

<sup>1</sup> "Testing of Chemical Reagents," 3 ed., p. 60.

<sup>2</sup> "Chemical Reagents, Their Purity and Tests," p. 80.

<sup>3</sup> "Ausgewählte Methoden d. Anal. Chem.," Erster Band, p. 835.

<sup>4</sup> In this connection, it is interesting to note that magnesium is occluded less by precipitating barium sulfate than any other metal which has been studied. Allen and Johnston, *J. Am. Chem. Soc.*, **32** (1910), 612; Johnston and Adams, *Ibid.*, **33** (1911), 832.

<sup>5</sup> Merck and Company, "Blue Label Reagents."

<sup>6</sup> Requests for information on this point were ignored by an American maker.

<sup>1</sup> The average of the MgO contents of the calcium carbonates given in Table II.

<sup>2</sup> *Orig. Com. 8th Intern. Congr. Appl. Chem.*, **1**, 217; *J. Am. Chem. Soc.*, **35** (1913), 867.

<sup>3</sup> Compare the method of analysis of high-grade zinc by F. Mylius and O. Fromm, in which they concentrate the impurities into a sulfide precipitate containing very little zinc. *Z. anorg. Chem.*, **9** (1895), 149.

<sup>4</sup> This need be weighed only to 5 per cent. The amount to be used depends on the MgO content of the salt. Cf. *postea*.



of calcium oxide to be added to the chloride solution. The calcium oxide must be added in amount somewhat more than sufficient to saturate the solution with respect to calcium hydroxide, and to precipitate the magnesium as hydroxide. From the data of Zahorsky<sup>1</sup> and of Lunge,<sup>1</sup> we find that 100 cc. of a 10 per cent calcium chloride solution will dissolve 0.13–0.14 gram calcium oxide at 80° to 100°. One gram of calcium carbonate yields 0.560 gram calcium oxide, and for the precipitation of 1 gram magnesia there is required 1.392 grams calcium oxide. These figures, together with the solubility, show that the calcium oxide made from 0.5 gram calcium carbonate will saturate the solution and is in slight excess over that required to precipitate 0.100 gram MgO—equal to 1 per cent on a 10 gram sample. Similarly, calculation shows that 0.4 gram calcium carbonate will precipitate 0.6 per cent MgO in a 10 gram sample, and 0.3 gram calcium carbonate will precipitate 0.2 per cent MgO. It is obviously of great advantage to use the smallest possible amount of calcium oxide in this precipitation, and, for most salts, the oxide from 0.3 gram calcium carbonate suffices.

II. SOLUBILITY OF MAGNESIUM HYDROXIDE IN CALCIUM CHLORIDE SOLUTIONS SATURATED WITH CALCIUM HYDROXIDE—No information on this subject has been found in the literature. We have qualitatively estimated the effect of this solubility on the method, and have concluded that it is nearly negligible. The tests were made by determining the magnesia in 10 gram portions of a certain sample of calcium chloride, keeping all conditions constant except the volume of the solution in which the magnesium hydroxide was precipitated. This volume was varied from 25 cc. to 200 cc. The results showed that the change of solubility with increasing dilution is, fortunately, small. We have accordingly chosen the 10 per cent dilution as a convenient volume in which to work and one in which the error due to solubility is probably not over 0.2 mg. MgO for 100 cc.

This crude method of investigating the solubility of magnesium hydroxide in solutions of calcium chloride saturated with calcium hydroxide was made necessary on account of the difficulty of obtaining calcium salts free from magnesium and magnesium salts free from calcium. It was thought to be beyond the scope of this paper to prepare suitable materials and actually determine this solubility. One experiment on the solubility of magnesium hydroxide in calcium hydroxide solution saturated at 90° was made by determining the magnesium in the liquid phase after having removed the calcium as sulfate. The magnesia in 100 cc. of this solution is probably less than 0.1 mg., since the precipitate of ammonium magnesium phosphate was too small to be filtered off and weighed.

III. USE OF SODIUM HYDROXIDE AS THE PRECIPITANT—It is obvious that a known amount of sodium hydroxide may be used to precipitate the magnesium and a slight excess of calcium hydroxide. Where acid has been used to bring a calcium salt into solution,

the excess acid is carefully neutralized, using methyl orange as indicator, and then an amount of sodium hydroxide solution is added, sufficient to precipitate the magnesium and a slight amount of calcium hydroxide. From this point on, the procedure is exactly as outlined under the calcium oxide precipitation.

In the work of Hildebrand and Harned quoted above, it is mentioned that the change in hydrogen ion concentration when the magnesium hydroxide has all been precipitated and the calcium hydroxide is beginning to precipitate, is too gradual to be shown by an indicator. Nevertheless, it was hoped that an indicator could be found by the change of which an indication would be given, when sodium hydroxide was used, that the hydrogen ion concentration corresponding to a precipitation of some small amount of calcium hydroxide had been reached. Several indicators of appropriate turning point ( $10^{-12}$  to  $10^{-13}$ ) were tested, but the results obtained were erratic. This was partly due to the fact that there are comparatively few indicators giving sharp color changes in this region of hydrogen ion concentration, and very probably also that there was a large "salt effect" due to the highly concentrated calcium chloride solution.

THE PRECISION OBTAINABLE by the hydroxide concentration method, and the agreement between it and the sulfate separation, are shown in Table I.

TABLE I.—PERCENTAGES OF MAGNESIA

Sample	By hydroxide concentration	By sulfate separation
A	0.091	0.074
	0.091	0.090
	0.089	...
	0.090	...
B	0.25	0.25

These analyses on carefully mixed samples of calcium carbonate were run side by side. On still another sample of calcium carbonate, the writer obtained 0.09 per cent MgO, using the new method with but one precipitation of the oxalate, while Dr. H. S. Washington, of this laboratory, found 0.12 per cent MgO, using the same method but making two careful precipitations of the calcium oxalate. The difference is about what would be occluded by the first precipitate of calcium oxalate.

NOTES ON THE METHOD—Since the effect of the salts of other acids on the solubility of magnesium hydroxide in calcium chloride solutions saturated with calcium hydroxide has not been determined, it is advisable to ignite such calcium salts as the nitrate, acetate, formate, and oxalate to oxide, and then dissolve all but a portion equivalent to the 0.3–0.5 gram of CaCO<sub>3</sub>, in dilute hydrochloric acid, using methyl orange as indicator. The reserved portion of oxide is added as the precipitant, thus removing the possibility of introducing magnesium as an impurity in the calcium oxide made from calcium carbonate, or in the sodium hydroxide. The carbonate, hydroxide, oxide, sulfite, and sulfate should be dissolved directly in hydrochloric acid.

Traces of calcium as tricalcium phosphate are frequently present to the extent of some 0.3–0.5 mg. in

<sup>1</sup> As given by Seidell, "Solubilities of Inorganic and Organic Substances," p. 91, 1st ed.

the magnesium pyrophosphate, and may be corrected for by dissolving the ignited (and weighed) precipitate in a little dilute sulfuric acid, adding alcohol, and allowing to stand over night. The calcium sulfate is filtered off and weighed as such; or it may be converted into oxalate and weighed as oxide.

It is obvious that there is practically no limit to the size of the sample from which the magnesium can be concentrated by this method, thus allowing almost any desired precision in the amount of magnesium weighed. A 10 gram sample will permit of 0.001 per cent MgO being

on the magnesia content of *all* the samples tested by the new method. As will be seen by an inspection of the table, these samples are from all of the more widely known makers of analyzed chemicals. In presenting these results there is absolutely no discrimination, and we think that a comparison of the makers' determinations as given in the table will support our statement that all the makers are equally at fault in this particular. We publish these data not as a criticism of the makers, but solely to present the facts in the case as we find them, with the hope that their publication

TABLE II MAGNESIA FOUND IN HIGH GRADE CALCIUM SALTS FROM DIFFERENT MAKERS

SALT	MAKER	DESCRIPTION	LOT NO.	Maker's analysis	MAGNESIUM OXIDE	
					Hydroxide concentration method	MgO calc. as per cent of CaO
Acetate.....	B & A	"C. P."		No anal.	0.027%	0.076%
Acetate.....	E & A	"Tested Purity"	B 83	-0.001%	0.041	0.11
Acetate.....	J T B	"C. P." Analyzed	51313	-0.001	0.001	0.002
Carbonate.....	B & A	"C. P." Analyzed		"Trace"	0.090	0.16
Carbonate.....	B & A	"C. P." Analyzed		No anal.	0.25	0.44
Carbonate.....	B & A	"Special"		No anal.	-0.001	0.00
Carbonate.....	J T B	"C. P." Analyzed	8212	0.001	0.039	0.068
Carbonate.....	J T B	"C. P." Special		-0.001	0.048	0.085
Carbonate.....	J T B	"C. P." Analyzed	101212	0.001	0.056	0.10
Carbonate.....	J T B	"C. P." Analyzed	5513	0.005	0.027	0.048
Carbonate.....	J T B	"C. P." Analyzed	101613	0.005	0.10	0.17
Carbonate.....	E & A	"Tested Purity"	B 33	0.005	0.27	0.48
Carbonate.....	Kb	"Zur Anal. m. Garantieschein"	4782	0.000	0.062	0.11
Carbonate.....	M	"Blue Label Reagent"	10853	Free	-0.001	0.00
Carbonate.....	M	"Blue Label Reagent"	12303	Free	0.000	0.000
Carbonate.....		Iceland Spar			0.047	0.084
Chloride.....	B & A	"C. P." Fused Granular		"Trace"	0.058	0.11
Chloride.....	J T B	"C. P." Analyzed Cryst	103012	0.001	0.009	0.023
Chloride.....	J T B	"C. P." Analyzed Cryst. (Diff. Bottle)	103012	0.001	0.006	0.015
Chloride.....	J T B	"C. P." Analyzed Anhyd.	10912	0.001	0.042	0.083
Chloride.....	J T B	"C. P." Analyzed Anhyd.	11612	0.001	0.15	0.29
Chloride.....	J T B	"C. P." Analyzed Anhyd. (12-mesh)	121812	0.005	1.44	2.85
Chloride.....	J T B	"C. P." Analyzed Anhyd.	112112	0.01	0.23	0.45
Chloride.....	J T B	"C. P." Analyzed Cryst.	122211	0.002	0.065	0.17
Chloride.....	M	"Blue Label Reagent" Fused	10353	Not det.	0.023	0.045
Formate.....	J T B	"C. P." Analyzed	61812	None	0.005	0.038
Hydroxide.....	J T B	"Technically Pure"	32213	0.05	0.87	1.14
Hydroxide.....	M	"Blue Label Reagent"	1472	Not det.	0.68	0.89
Nitrate.....	J T B	"C. P." Analyzed Cryst.	101712	0.001	0.14	0.59
Nitrate.....	E & A	"Tested Purity"	B 13	None	0.31	1.31
Oxalate.....	Kb	White Label	L 2891	No anal.	0.041	0.084
Oxide.....	J T B	From Marble	32413	0.51	1.18	1.18
Oxide.....	Kb	"Zur Anal. m. Garantieschein"		Not det.	0.77	0.77
Sulfate.....	M	"Blue Label Reagent"	11513	Free	0.007	0.021
Sulfite.....	E & A	"Tested Purity" Cryst.	B 83	0.05	0.36	1.00

## ABBREVIATIONS

B & A: Baker & Adamson Chemical Company, Easton, Pa.  
 J T B: J. T. Baker Chemical Company, Phillipsburg, N. J.  
 E & A: Eimer & Amend, New York, N. Y.  
 Kb: C. A. F. Kahlbaum, Berlin.  
 M: Merck & Company, New York, N. Y.

No anal.: No analysis on label.

Not det.: Analysis on label but MgO not determined.

Free: Free from MgO as tested by Krauch's method.

-0.001: Less than 0.001% MgO.

approximately determined. We have used at times samples of 20 and even 100 grams with this method.

The oxalate separation has been used after the hydroxide concentration in order to combine in one precipitation the removal of calcium and also the slight amounts of iron and aluminum which may be present. While the sulfate separation is undoubtedly the better, it requires an evaporation and a separate precipitation for the other impurities.

RESULTS OBTAINED BY THE HYDROXIDE CONCENTRATION METHOD—In Table II are given the results

may help to bring about the more complete elimination of magnesia from calcium salts, and hence to help raise the standard of analyzed chemicals. We think that in presenting the matter in this way, it is fairest both to the maker and to the user. With this presentation of the subject, our direct interest must end, since, as stated at the beginning, the problem was but a mere side issue, and further testing of calcium salts on our part has been rendered unnecessary, as we have secured by purchase enough of the purest of the lots tested to last us several years.

For many purposes where the highest grade calcium salts are used, the presence of much magnesia may be regarded as a matter of indifference. The two elements are chemically very similar; the reactions of one may not interfere with those of the other. Whether the presence of magnesium in calcium salts is objectionable for certain purposes or not is, however, aside from the main issue. The point to be emphasized is that the makers' analyses should represent exactly the amounts of impurities present. Only in this manner can the makers' analyses be of any real service to the user of analyzed chemicals.

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### PARAFFIN BODIES IN COAL TAR CREOSOTE AND THEIR BEARING ON SPECIFICATIONS<sup>1</sup>

By S. R. CHURCH AND JOHN MORRIS WEISS

In specifications for coal tar creosote, there is usually a paragraph stating that the oil shall be a pure product of coal tar, and free from adulteration with any oil or products from any other tar. The purpose of this clause is usually to provide against admixture with petroleum products, such as water gas tar or oil tar derivatives. In the present paper, the writers wish to consider one requirement which is sometimes introduced with the object of enforcing this provision.

Coal tar is made up mainly of aromatic compounds, and the presence of bodies belonging to the saturated paraffin series has been regarded by some as direct and unmistakable evidence of contamination of coal tar creosote by distillates from other tars.

Dean and Bateman<sup>2</sup> proposed a sulfonation test for creosote oils, based on the principle that aromatic hydrocarbons dissolve in concentrated sulfuric acid to sulfonic acids, while bodies of the paraffin series remain unattacked. They applied this test to numerous creosote oils, and concluded that any oil yielding a sulfonation residue was contaminated with products of other source than coal tar.

A modification of this test, devised by J. M. Weiss, was proposed in an article by S. R. Church,<sup>3</sup> which did not in any way change the results of the test, but merely made it easier of operation, so far as the detection of traces was concerned. Later Bateman<sup>4</sup> made further modifications in the test, which made it a still more convenient laboratory operation. This modification was endorsed by Church<sup>5</sup> after trial, as more convenient and practical than the earlier proposals.

Chapin<sup>6</sup> proposed the substitution of a dimethyl sulfate test to be used to determine paraffin hydrocarbons in creosote oil, as well as in creosote oil dips.

<sup>1</sup> Presented before the American Association for the Advancement of Science, Engineering Section, Atlanta, December 31, 1913.

<sup>2</sup> Dean and Bateman, "The Analysis and Grading of Creosotes," Forest Service, Circular 112.

<sup>3</sup> Church, This Journal, 3 (1911), 225.

<sup>4</sup> Bateman, "Modification of the Sulfonation Test for Creosote," Forest Service, Circular 191.

<sup>5</sup> Church, This Journal, 5 (1913), 195.

<sup>6</sup> Chapin, "Dimethyl Sulfate Test for Creosote Oils and Creosote Dips," Bureau of Animal Industry, Circular 167.

Reeve and Lewis<sup>1</sup> have used this test, and have given a number of results obtained by it.

A brief description of the tests in question may be useful in this connection.

#### SULFONATION TEST

"Ten cubic centimeters of the fraction of creosote to be tested are measured into a Babcock milk bottle. To this is added 40 cc. of 37 N sulfuric acid, 10 cc. at a time. The bottle with its contents is shaken for two minutes after each addition of 10 cc. of acid. After all the acid has been added, the bottle is kept at a constant temperature of from 98° to 100° C. for 1 hour, during which time it is shaken vigorously every ten minutes. At the end of an hour, the bottle is removed, cooled and filled to the top of the graduation with ordinary sulfuric acid, and then whirled for 5 minutes in a Babcock separator. The unsulfonated residue is then read off from the graduations."

#### DIMETHYL SULFATE TEST

"Five cubic centimeters of the fraction are pipetted into a narrow 25 cc. burette, and shaken with 8 cc. of dimethyl sulfate after closing the burette with a smooth, close-fitting cork. Separation of the residual oil occurs in a short time in the form of a clear, almost colorless, supernatant liquid layer."

We shall first briefly discuss the relative merits and demerits of the sulfonation test and the dimethyl sulfate test, and then consider in what manner the results of such a test should be interpreted, particularly as regards creosote oil specifications.

We have made some experiments using the dimethyl sulfate test, as recommended by Chapin, and the modified sulfonation test with fuming sulfuric acid and the Babcock bottle, as proposed by Bateman. Average samples of coal tar oil and water gas tar oil were distilled, and fractions taken from 240° to 270° C., and from 270° to 300° C. These fractions were then subjected to the dimethyl sulfate test and the sulfonation test, with the following results:

	Sulfonation test residue Per cent	Dimethyl sulfate test residue
Coal tar distillate 240-270° C. ....	1.2	0
Coal tar distillate 270-300° C. ....	2.0	0
Water gas tar distillate 240-270° C. ....	4.0	0
Water gas tar distillate 270-300° C. ....	6.8	0

Further tests on other oils were also made, with the following results:

	Sulfonation test residue Per cent	Dimethyl sulfate test residue Per cent
Water gas tar distillate 240-270° C. ....	2.4	0.0
Water gas tar distillate 270-330° C. ....	1.2	0.0
Mixed tar distillate 240-270° C. ....	2.0	0.0
Mixed tar distillate 270-330° C. ....	3.0	0.0
Blast furnace tar distillate 240-270° C. ....	17.6	23.0
Blast furnace tar distillate 270-330° C. ....	23.2	38.0
Oil tar distillate 240-270° C. ....	14.4	22.0
Oil tar distillate 270-330° C. ....	18.8	28.0

It can be seen from these results that the dimethyl sulfate method showed no residue in many oils that

<sup>1</sup> Reeve and Lewis, This Journal, 5 (1913), 293



gave measurable residues by the sulfonation method, and we feel that the former test is of no value so far as the detection of small amounts of saturated hydrocarbons in the presence of aromatic hydrocarbons is concerned. Undoubtedly, if there were considerable amounts of petroleum or blast furnace tar distillates present, where there might be a sulfonation residue of from 10 to 20 per cent, the dimethyl sulfate test would detect it, but where there is only a question of comparatively small admixtures of material, itself low in sulfonation residue, this test would not seem to be of any value.

We have experienced great difficulty in obtaining dimethyl sulfate; moreover, we find that it changes rapidly on standing, so that fresh supplies must frequently be had. Another objection to this reagent is the danger attendant upon handling it.

In a great deal of our laboratory work on oils distilled from various kinds of tar, the results have been clouded by uncertainty as to the authenticity of the sample. Some time ago, therefore, we procured samples of tars from typical coke ovens and gas plants

above. In the appended table are given the results of these tests of the various oils examined, representative tests of each type of installation being selected. Where there were any great variations between oils of the same origin, the tests of the two most widely divergent materials examined are given.

A consideration of the creosote oil specifications in active use indicates a tendency toward the use of the sulfonation test. The requirements of the test vary widely; in one case, the sulfonation residue is limited to 10 per cent, in others to 1 per cent, while still others specify that in the fraction 300° to 360° C. it shall not exceed 0.25 cc.

In a Forest Service circular, C. P. Winslow<sup>1</sup> gives the requirement for Class 1 and Class 2 coal tar creosotes (the only ones considered by him as pure coal tar creosotes) that there shall be no sulfonation residue. In "mixed coal tar creosotes," he allows, in Class 1, 10 per cent of the 305–320° C. fraction as a sulfonation residue, and in Class 2, 20 per cent of the fraction 305–320° C., expressing it in the form that "the volume of the sulfonation residue in cubic centimeters should

OILS DERIVED FROM	Up to 210°	210– 225°	225– 235°	235– 245°	245– 255°	255– 265°	265– 275°	275– 285°	285– 295°	295– 305°	305– 320°	320– 330°
Semet-Solvay coke oven tar.....	0	0	0	0	0	0	0	0	0	0	0	0
Koppers coke oven tar.....	0	0	0	0	0	0	0	0	0	0	0	0
United Otto coke oven tar.....	0	0	0	0	0	0	0	0	0	0	0	0
Horizontal gas retort tar.....	0.2	0.2	0.4	0.6	0.8	0.8	0.8	0.8	0.8	0.4	0.4	0.4
Inclined gas retort tar.....	2.0	2.0	2.0	4.0	5.6	6.4	5.2	6.4	6.0	5.6	5.2	4.0
Vertical gas retort tar.....	5.8	3.6	3.6	4.6	5.6	5.6	6.2	4.8	6.0	4.0	4.4	2.2
Water gas tar, 1.....	0.4	0.4	0.4	0.4	0.4	0.8	0.8	0.8	0.8	0.8	0.4	0.4
Water gas tar, 2.....	3.2	5.2	6.0	6.4	7.2	9.2	10.4	10.0	14.2	13.6	13.6	12.4
Oil tar.....	9.2	22.8	26.4	26.4	26.0	33.2	31.6	35.6	42.4	36.0	32.0	32.0
Blast furnace tar.....	...	11.6	14.4	16.4	17.2	20.4	21.2	22.0	20.8	20.4	18.0	16.4
Lignite tar.....	7.0	7.0	9.8	11.6	13.4	14.8	17.0	20.4	20.4	19.6	19.0	12.0

under such conditions as to make accidental contamination or admixture practically impossible. These tars were distilled to pitch, and the distillate oils recovered. The oils were subjected to a number of tests, partially along the lines of Dean and Bateman's work (*loc. cit.*). It is not our intention to give the details of this work at present, except in so far as they affect the question of the sulfonation test.

Coal tars may be divided into two classes:

1—Coke oven tars, which may be further subdivided according to the type of oven in which the coal is carbonized,

2—Gas works tars, which may be divided similarly into horizontal, inclined and vertical gas works tars.

In this investigation, we had one or more samples from each of the different types of installation, both coke oven and gas works, and have, we believe, examined a sufficient number of samples to draw correct conclusions.

The examination of the oils, which is of interest in this connection, was a Hempel distillation (made in accordance with the Forest Service method for analysis of creosote oil), taking fractions at the following temperatures, Centigrade:

210	235–245	265–275	295–305
210–225	245–255	275–285	305–320
225–235	255–265	285–295	320–330

These fractions were then subjected to the sulfonation test, using Bateman's modified method, as described

not be greater than one-tenth or one-fifth, respectively, of the weight of the fraction in grams."

In the opinion of the writers, the requirement of no sulfonation residue is unfair as a basis of classification of pure coal tar creosotes, and a very high limit for mixed creosotes, such as 10 to 20 per cent, is useless, in view of the fact that a great majority of the water gas tar distillates have considerably less than this amount of sulfonation residue in any fraction, and this makes it unnecessary, *per se*, to have any coal tar creosote at all present. If a requirement for no sulfonation residue should be enforced, only straight coke oven tars could be used to produce such creosote oils, and in most cases this is certainly a commercial impossibility. If a limit of 1 per cent is set, the coke oven tar oils and some of the horizontal gas works tar oils would meet the requirement, but some of the latter would require the admixture of coke oven tar oils to bring the residue below this limit. A requirement that the sulfonation residue shall not exceed 2 per cent would not be unfair, and would not ordinarily bar any normal coal tar creosote oils. It would prevent the addition to coal tar creosotes of large proportions of blast furnace oils and petroleum products other than those from water gas tar. The admixture of water gas tar distillates with coal tar creosote oil would, of necessity, have to be taken care of in some other way than by the sulfonation test, as it is very plain that cer-

<sup>1</sup> Winslow, "Commercial Creosotes," Forest Service, Circular 206

tain mixtures of coke oven tar oil and water gas tar oil would show a lesser residue than certain other oils obtained wholly from gas works coal tars.

In conclusion, the authors believe that the sulfonation test in itself has been shown to be of comparatively little value in detecting the admixture of oils of petroleum origin, particularly those derived from water gas tar, with creosote oil.

In a later paper, we hope to publish additional data from our analyses of authentic tars, indicating the value of certain other tests as means for determining the origin of oils used for creosoting.

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### A VOLUMETRIC METHOD FOR THE DETERMINATION OF LEAD

By ALFRED ALDER AND M. F. COOLIDGE

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The principles of the determination are based upon the precipitation and separation of the lead as sulfate, the solution of this precipitate in sodium hydroxide and the precipitation of the lead from the solution, after slightly acidifying it with nitric acid, by a solution of potassium iodate. The precipitate of lead iodate is dissolved in dilute hydrochloric acid. It is then titrated in the presence of a few cubic centimeters of chloroform, with a standard solution of ammonium sulfocyanate to the first appearance of a violet color in the chloroform.

The outline scheme for the analysis of an ore is as follows: Treat 0.5 to 1 gram with nitric acid, and, if necessary, with a small quantity of hydrochloric acid. Then add a few cc. of sulfuric acid and evaporate to dense fumes of sulfuric anhydride, leaving not more than 2 to 3 per cent of free sulfuric acid present when the solution is diluted to 100 cc. Cool the thoroughly decomposed material and add about 100 cc. of water, bring to a vigorous boil and add 10 to 15 cc. of alcohol. Cool and allow to stand until the precipitate has completely settled, and then decant upon a filter paper and wash the residue with a mixture of 1 per cent sulfuric acid and 10 per cent alcohol, and finally with the alcohol alone. Dissolve the lead sulfate in a small quantity of hot sodium hydroxide (10 to 15 cc. of a 10 per cent solution will usually be sufficient). Wash the residue and filter paper thoroughly with hot water, followed by hot water slightly acidified with nitric acid and finally by water slightly alkaline with sodium hydroxide. Add a few drops of phenolphthalein to the solution and a quantity of potassium iodate solution sufficient to precipitate all of the lead and have a small amount in excess. Heat the solution, and while hot add nitric acid (1.2 sp. gr.), drop by drop, until the pink of the phenolphthalein is discharged, and then 15 to 29 drops in excess. Bring the whole to a boil, cool slightly, add 15 to 20 cc. of alcohol and then cool to room or tap water temperature. Decant the solution through a filter paper and wash by decantation with one part of alcohol to three parts of water until the wash solution gives no test for iodate when treated with hydrochloric acid, chloroform and ammonium

sulfocyanate. Transfer the filter paper and precipitate to a 250 cc. stoppered flask. Wash out the precipitation vessel with 40 to 50 cc. of a cold solution of hydrochloric acid (1 vol. conc. HCl to 2.5 vols. water) and transfer to the flask with the main portion of the precipitate. Add 3 to 5 cc. of chloroform to the above solution and titrate at once with the standard ammonium sulfocyanate to the first violet which remains in the chloroform after vigorous shaking. For ores high in lead it is advisable to add to the flask before the end point is reached 10 to 15 cc. of cold HCl (1.1 sp. gr.).

#### NOTES ON THE DETERMINATION

The above method was tested out with purified lead sulfate and gave the following results:

G. PbSO <sub>4</sub> taken	G. Pb in PbSO <sub>4</sub>	G. Pb found	G. PbSO <sub>4</sub> taken	G. Pb in PbSO <sub>4</sub>	G. Pb found
0.3	0.2049	0.2047	0.3	0.2049	0.2046
0.3	0.2049	0.2038	0.3	0.2049	0.2044
0.3	0.2049	0.2056	0.3	0.2049	0.2045
0.3	0.2049	0.2052	0.4	0.2732	0.2728
0.3	0.2049	0.2049	0.2	0.1366	0.1369
0.3	0.2049	0.2051	0.1	0.0683	0.0684
0.3	0.2049	0.2049			

A number of ores were run by this method using 0.5 gram samples for the determinations. The lead in these ores had been previously determined by a careful analysis, weighing up the lead as the sulfate. The following are some of the results obtained:

No. ore	Lead by PbSO <sub>4</sub> method	Lead by iodate method
	Per cent	Per cent
1.....	3.18	3.26
2.....	4.20	4.18
3.....	4.42	4.37
4.....	50.51	50.6
5.....	64.39	64.27

Ammonium acetate, sodium acetate and potassium hydroxide, as well as the sodium hydroxide were used in the solution of the lead sulfate obtained from the decomposition of the ore, or that which was used as the standard. From the ammonium acetate or sodium acetate solutions, either neutral or acid with acetic acid, the lead iodate precipitated slowly and incompletely. Boiling, long standing and a decided excess of potassium iodate tended to make the precipitation complete, but under most careful conditions gave quite decidedly low results. The potassium hydroxide gave equally as good results as the sodium hydroxide. It is difficult to wash the filter paper free from the solution obtained by the treatment of the lead sulfate with the sodium hydroxide. Experiments gave results as much as 10 per cent low. This difficulty is corrected by washing with dilute nitric acid followed by washing with a dilute solution of sodium hydroxide.

The solubility of lead iodate is given as 0.012 gram in a liter of water at 2° C. and 0.019 gram in a liter of water at 18° C. (Kohlrausch and Böttger). It is stated that its solubility in nitric acid is only slight, some authorities going so far as to say that it is insoluble in hot dilute nitric acid. Experiments were made to test this point. The precipitates of lead iodate were washed with hot dilute nitric acid and the lead content determined. The same was repeated using

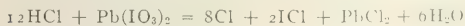
the cold dilute acid. The following are a few of the results obtained:

Lead taken: 0.2049 gram  
Lead found: 0.1969, 0.1995, 0.1957 and 0.1971 gram

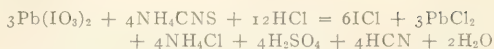
When water was used to wash the precipitate, low results which would not agree with each other were obtained. In washing with nitric acid or water, the wash water could not be freed from iodate as given by the test with hydrochloric acid, chloroform and ammonium sulfocyanate. The solubility of the lead iodate in dilute  $\text{HNO}_3$  with a slight excess of potassium iodate and alcohol present was shown by evaporating the filtrates from seven solutions out of which the lead had been precipitated as iodate according to the outline scheme. The original solutions contained 1.7 grams of lead. The solutions which were evaporated were fumed with  $\text{H}_2\text{SO}_4$  and the lead determined as sulfate according to the regular method. The amount of lead sulfate found was 0.6 mg.

If lead iodate is precipitated in the cold it comes down in a flocculent form and is not readily purified. Unless an extra amount of time is taken in the washing the results will be high, due to the retention by the precipitate of some of the excess of potassium iodate. When the lead is precipitated hot, or boiled after precipitation it comes down with a coarsely crystalline structure. The precipitate settles rapidly and is readily purified from the excess iodate. Forty to fifty cc. of the alcoholic solution have proved ample for washing, even when 0.25 gram of lead in the form of iodate was being treated. Too much alcohol added to the solution at the precipitation of the lead iodate, or too strong an alcoholic solution used for washing purposes will make the removal of the excess of potassium iodate difficult, since this substance is much less soluble in alcohol than in water. Too much potassium iodate should not be added in excess because of the expense of the reagent, and the added difficulty of washing it out. It is important that the solution from which the lead is precipitated as iodate should be made distinctly acid with  $\text{HNO}_3$ , otherwise some lead will be present as the hydroxide and the results will be low. Lead iodate is decidedly soluble in an excess of a fixed alkali hydroxide.

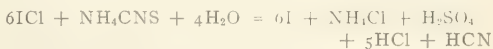
The lead iodate is soluble in dilute cold hydrochloric acid without the decomposition of the iodate radical. If the hydrochloric acid is concentrated or the dilute solution hot, chlorine will be liberated and the iodate radical decomposed. This reaction can possibly be represented by the following equation:



Whenever chlorine is liberated, the determination is ruined since the results will be decidedly low. The strength of hydrochloric acid used in the outline scheme will not liberate chlorine unless the solution is hot. The reaction between the lead iodate and the  $\text{NH}_4\text{CNS}$  is most rapid when the iodate is completely in solution. If, after the titration has been started, it is noticed that some of the iodate is not in solution, it is best to add more of the hydrochloric acid. The reaction of titration is:



The end point is caused by the liberation of the I from the ICl and its absorption in the chloroform. The equation for the end point is probably the following:



When sufficient hydrochloric acid is present the reaction of titration is a very rapid one, and the end point very sharp and distinct, leaving nothing to be desired in that direction. The approach to the end point is indicated by the rapidity of the discharge of a yellowish red color throughout the solution. The end point can, in fact, be determined quite closely even without the use of chloroform, by the permanent formation of this yellowish red color. The chloroform can be used over again by decanting off the larger portion of the filter paper pulp and solution and then adding the precipitate from another determination.

The ammonium sulfocyanate is made by dissolving about 2.5 grams of the pure salt in a liter of water and then standardizing it according to the well known Volhard method for silver by titrating a known silver nitrate solution which has been made by dissolving pure silver in nitric acid and boiling off the nitrous fumes. The silver standard of the ammonium sulfocyanate multiplied by 1.4398 gives the lead standard. The  $\text{NH}_4\text{CNS}$  may also be standardized by titration against c. p. lead sulfate or metallic lead. The above strength of solution will equal about 1 per cent of lead for each cubic centimeter when 0.5 gram sample is taken for analysis.

The elements encountered in the ordinary ore analysis which might interfere with the determination of the lead by giving insoluble iodates are barium, calcium, copper, silver, bismuth, mercury and ferric iron. Of these only the barium, calcium, silver and bismuth are likely to interfere since the copper and mercury can be completely removed and the ferric iron nearly removed from the lead by filtering them off from the insoluble lead sulfate formed in the decomposition of the ore. The solutions must contain calcium in rather large concentration before this element will precipitate as iodate under the conditions given for the lead determination. In no experiment tried was it found to interfere with the accuracy of the method for lead. Barium forms an insoluble iodate which is slightly soluble in dilute nitric acid, but barium sulfate is not affected by sodium hydroxide and only very slightly by dilute nitric acid, so that not enough of it is carried into solution to be precipitated as the iodate. Experiments with these two elements show their influences upon the determination.

G. $\text{PbSO}_4$ taken	G. $\text{BaSO}_4$ taken	G. $\text{CaSO}_4$ taken	G. Pb in $\text{PbSO}_4$	G. Pb found
0.3	0.1		0.2049	0.2052
0.3	0.2		0.2049	0.2046
0.3	0.2	0.1	0.2049	0.2042

It is difficult by the ordinary methods of treatment to remove all the silver and bismuth from the insoluble



lead sulfate precipitate. These elements form, when treated with sodium hydroxide solution, insoluble silver oxide and bismuth hydroxide which are readily soluble in dilute nitric acid. To keep these from going in with the lead solution, and at the same time to purify the filter paper from the lead, it was found necessary, after the filtration of the solution obtained by the treatment of the lead sulfate with the sodium hydroxide, to remove the filtrate and treat the residue and filter paper with hot water slightly acidified with nitric acid. The filtrate obtained by this treatment is made quite strongly alkaline with sodium hydroxide and filtered through the same filter paper. From the combined filtrates the lead iodate is precipitated. The following experiments show that these elements, when the treatment is made according to the above modifications of the outline scheme, have no effect upon the accuracy of the results. Ferric iron is not readily precipitated as the iodate in presence of nitric acid also has no effect upon the results.

G. PbSO <sub>4</sub> taken	G. Ag <sub>2</sub> SO <sub>4</sub>	G. Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	G. Bi <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	G. Pb in PbSO <sub>4</sub>	G. Pb found
0.3	0.1	...	0.1	0.2049	0.2047
0.3	0.1	...	0.1	0.2049	0.2043
0.3	...	0.015	...	0.2049	0.2051

The determination of lead in an ore by this method can be made in 45 minutes to one hour's time. The cost of the reagents in the determination is not excessive, and should not exceed a few cents per determination when 0.5 to 1 gram samples are used. For low-grade lead ores the cost is materially reduced because of the smaller quantity of potassium iodate required. Some of the advantages of the determinations are rapidity of manipulation, definiteness of the reactions of titration, non-interference of the elements usually associated with lead minerals and exactness of the end point.

SOUTH DAKOTA STATE SCHOOL OF MINES  
RAPID CITY

## THE DETERMINATION OF ARSENIC IN HYDROCHLORIC AND SULFURIC ACIDS

By R. F. TARBELL

Received January 22, 1914

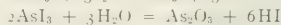
It is always necessary in the manufacture and purchase of hydrochloric and sulfuric acids that are to be used in the preparation of food products to make some sort of test to determine the percentage of arsenic present.

The writer has worked out a method which he has found very satisfactory and accurate. Once the apparatus is set up and the standard solutions and reagents prepared, a determination requires very little attention.

### PRINCIPLES INVOLVED

It is well known that arsine and iodine react together under certain conditions forming arsenious iodide. This reaction seems to hold when the iodine is dissolved in specially prepared gasoline. In the following method arsine is generated in the usual way, passed through a solution of lead acetate to remove any hydrogen sulfide formed and then passed through a

known volume of an iodine-in-gasoline solution of known strength. The excess of iodine is reduced by adding a known amount of a sodium arsenite solution and then titrated back with an iodine solution using starch as indicator. The writer has found that by this method one atom of arsenic is equivalent to eight atoms of iodine. This would correspond to the following equations:



### APPARATUS

A train is connected as follows: A 500 cc. flask is fitted with a two-hole rubber stopper. Through one hole in the stopper is fitted a 125 cc. globe-shaped separatory funnel turned up at its lower end to prevent the escape of gas. Through the other hole is fitted a Kjeldahl connecting bulb. This is in turn connected with a Koeninck's potash bulb. The potash bulb is next connected to a single bulb such as always comes with and precedes a Meyer's bulb tube. To this is connected a Meyer's bulb tube. There should be at hand a 500 cc. Squibb's pear-shaped separatory funnel.

### REAGENTS AND STANDARD SOLUTIONS

**Gasoline**—A quantity of gasoline is prepared from ordinary 60° gasoline in the following way: Fill a gallon bottle three-fourths full of the gasoline and add 200 cc. c. p. sulfuric acid. Stir this eight or ten hours with air, let settle, pour off the gasoline into a similar bottle, add 200 cc. c. p. sulfuric acid as before and let stand several days with occasional shaking. Pour the gasoline from the acid, add a dilute solution of sodium hydroxide and agitate ten or fifteen minutes to neutralize all acid. Wash gasoline with water, let settle, and when clear it is ready for use.

**Stannous Chloride Solution**—Dissolve 25 grams c. p. tin in arsenic-free hydrochloric acid and evaporate almost to dryness. Take up with water and make up to 500 cc.

**Arsenic-free Hydrochloric Acid**—Dilute c. p. hydrochloric acid to sp. gr. 1.10, add a small amount of either copper sulfate or mercuric chloride and precipitate with hydrogen sulfide. Let stand four or five days, filter and distil.

**Alkaline Sodium Arsenite Solution**—Dissolve 0.2640 gram pure arsenious oxide and 1 gram sodium carbonate in 100 cc. hot water. After cooling, add 1 gram sodium bicarbonate and make total volume 1 liter with water.

**Iodine Solution**—Dissolve 0.6773 gram pure iodine and 1.2 grams potassium iodide in water and make the volume up to 1 liter.

**Iodine-in-Gasoline Solution**—Dissolve 0.6773 gram pure iodine in the prepared gasoline and make the volume up to 1 liter with gasoline.

**Zinc**—Use c. p. arsenic-free stick zinc.

### METHOD OF ANALYSIS

Fill the potash bulb with lead acetate solution to the top of the first bulb. Put 20 cc. iodine-in-gasoline

solution, 80 cc. gasoline and 20 cc. water into the bulb tubes. Place a stick of zinc weighing about 35 grams in the flask and connect the apparatus, seeing that all joints are tight. Weigh out about 25 grams of the acid to be tested. The weight of sample and the quantity of iodine-in-gasoline solution used will of course vary with the arsenic content of the acid, but a little experience will enable the operator to adjust these quantities. If hydrochloric acid, its specific gravity should be made about 1.10 by adding either water or arsenic-free hydrochloric acid as may be necessary. If sulfuric acid, its specific gravity should be made about 1.40 by adding either water or c. p. sulfuric acid as may be necessary. Pour the sample through the separatory funnel into the flask. Then pour 1 cc. stannous chloride solution through the funnel. Pour through enough water to wash the funnel. Close the stopcock and let the reactions proceed with all connections tight for about 2 hours, heating the flask on a water bath if the action becomes too slow. Then add 20 cc. c. p. sulfuric acid (sp. gr. 1.40) through the separatory funnel and allow the test to proceed for 1 hour more. Empty the contents of the bulb tube into the 500 cc. separatory funnel. Wash the bulb tube with water into the same funnel. Run out the water from below and add 20 cc. sodium arsenite solution to the contents of the funnel. Shake till the solution is colorless, allow to settle into two layers and draw off the lower layer into a white dish. Add starch indicator and titrate with the iodine solution in the regular way: 1 cc. iodine solution = 1 cc. sodium arsenite solution = 1 cc. iodine-in-gasoline solution = 0.0005 gram arsenic.

## RESULTS OBTAINED

Mg. As taken	Mg. I taken by As	Mg. As found	Mg. As taken	Mg. I taken by As	Mg. As found
0.02	0.34	0.02	0.50	6.73	0.50
0.02	0.27	0.02	0.50	6.42	0.47
0.05	0.61	0.04	1.00	13.45	0.99
0.05	0.74	0.05	1.00	12.90	0.95
0.10	1.15	0.08	1.88	25.12	1.85
0.10	1.42	0.10	2.50	34.07	2.51
0.25	2.98	0.22	3.75	50.58	3.73
0.37	4.86	0.36			

A number of analyses were made using different volumes of solutions of sodium arsenite of known strength. Kahlbaum's arsenious oxide was used in making these solutions. The numbers in the last column are obtained by multiplying the figures in the second column by 0.07382.

NATIONAL ZINC COMPANY  
KANSAS CITY, KANSAS

### ONE CAUSE OF LOW RESULTS IN THE ASSAY OF PEPPERMINT OIL

By HARRY W. REDFIELD

Received April 26, 1913

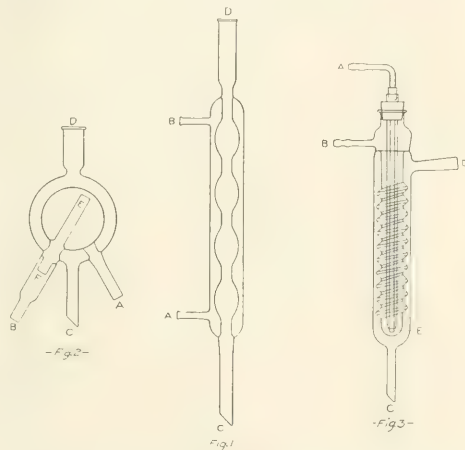
Articles in *Hygienic Laboratory Bulletin*, No. 49, "Digest of Comments on the Pharmacopoeia of the United States of America" (Eighth Decennial Revision), pages 222 and 223, and in *Hygienic Laboratory Bulletin* No. 75, "Digest of Comments on the Pharmacopoeia of the United States of America" (Eighth

Decennial Revision), pages 395 to 396, point out the fact that low results are often obtained in the assay of peppermint oil.

One possible source of error that seems to have received no attention is the low efficiency of the reflux condenser that is employed when the oil is boiled for one hour with a  $N/2$  alcoholic solution of potassium hydroxide, in the determination of menthol as ester; and later in the method when the oil is boiled for one hour with acetic acid anhydride, and also when the acetylated oil is boiled for one hour with a  $N/2$  alcoholic solution of potassium hydroxide, in the determination of total menthol. Any oil lost through incomplete condensation would, obviously, cause low results.

Therefore, a number of determinations of menthol as ester and of total menthol were made on six different samples of peppermint oil obtained from as many sources. The three forms of condenser illustrated were used.

In Fig. 1 is shown the Allihn condenser.



In Fig. 2 is shown the Chamot-Soxhlet glass ball condenser. The device at F is worthy of mention as it enables the experimenter to see at a glance how much water is flowing through the condenser.

In Fig. 3 is shown the Fritz Friedrichs condenser, which may be used as a reflux condenser by allowing the vapor to enter at C, or which may be used in distillations by allowing the vapor to enter at D. The water for cooling enters through AE and escapes through B.

EXPERIMENT 1—A peppermint oil was used that had a specific gravity of 0.9056 at 25° and showed a polarization of -19.87 at 25°. Equal volumes of the oil were weighed in three 125 cc. flasks and the required amounts of  $N/2$  alcoholic potassium hydroxide added. Into the neck of one of the flasks was inserted an Allihn condenser, into the neck of another was inserted a Chamot-Soxhlet condenser, and into the neck of the third was inserted a Fritz Friedrichs condenser. The outlet D of each condenser was loosely plugged with cotton wool. The condensers were connected in series,

the cooling water first flowing through the Fritz Friedrichs condenser, then through the Chamot-Soxhlet condenser and finally through the Allihn condenser. Heat was supplied under the flasks by small ring burners and the assay followed out according to the Pharmacopoeia method.

EXPERIMENT 2 was made on the same oil that was used in EXPERIMENT 1; the direction of the cooling water was reversed and it was made to flow first through the Fritz condenser and finally through the Fritz Friedrichs condenser. The purpose of this was to ascertain whether any advantage had been given to the Fritz Friedrichs condenser in the previous experiment, by reason of the fact that the temperature of the water flowing through the condensers was found to be  $2.1^{\circ}$  higher when it entered the Allihn condenser than it was when it entered the Fritz Friedrichs condenser, in the first experiment.

EXPERIMENT 3—A peppermint oil was used that had a specific gravity of 0.9002 at  $25^{\circ}$  and showed a polarization of  $-24.73$  at  $25^{\circ}$ . The condensers were connected in the same manner as in the first experiment.

EXPERIMENT 4—The same oil that was used in the third experiment was used again, and the condensers were connected in the same manner as in the second experiment, for the same reason.

EXPERIMENT 5—A peppermint oil was used that had a specific gravity of 0.9021 at  $25^{\circ}$  and showed a polarization of  $-20.37$  at  $25^{\circ}$ . The condensers were connected in the same manner as in the second experiment.

EXPERIMENT 6—A peppermint oil was used that had a specific gravity of 0.9045 at  $25^{\circ}$  and showed a polarization of  $-20.03$  at  $25^{\circ}$ . The condensers were connected in the same manner as in the second experiment.

EXPERIMENT 7—A peppermint oil was used that had a specific gravity of 0.8987 at  $25^{\circ}$  and showed a polarization of  $-24.88$  at  $25^{\circ}$ . The condensers were connected in the same manner as in the second experiment.

EXPERIMENT 8—A peppermint oil was used that had a specific gravity of 0.9010 at  $25^{\circ}$  and showed a polarization of  $-26.34$  at  $25^{\circ}$ . The condensers were connected in the same manner as in the second experiment.

The analytical results obtained in these eight experiments are given in the following table:

EXP. NO.	FRIEDRICHS CONDENSER		SOXHLET CONDENSER		ALLIHN CONDENSER	
	% menthol		% menthol		% menthol	
	As ester	Total	As ester	Total	As ester	Total
1.....	7.97	64.98	7.98	64.49	7.76	58.06
2.....	7.94	64.39	7.89	64.34	7.74	58.10
3.....	6.61	70.30	6.71	70.09	6.26	65.58
4..	6.59	69.23	6.57	69.20	6.23	64.97
5.....	9.33	63.74	9.28	63.59	9.02	60.20
6.....	8.23	60.19	8.17	60.07	7.84	55.72
7.....	8.97	69.42	9.07	69.26	8.59	64.57
8..	8.43	58.36	8.40	58.40	8.03	54.07
Average .....	8.01	65.08	8.01	64.93	7.68	60.21
Variation from max .....	0.00	0.00	0.00	0.18	0.33	1.87

#### SUMMARY

While the results obtained when using either the Fritz Friedrichs condenser or the Chamot-Soxhlet

condenser were almost the same, the results were 0.33 per cent low for menthol as ester and 4.87 per cent low for total menthol when the Allihn condenser was used.

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#### OBSERVATIONS UPON THE ASSAY OF DIGESTIVE FERMENTS<sup>1</sup>

By HOWARD T. GRABER

In a previous paper, "Some Observations upon the Assay of Digestive Ferments," appearing in *THIS JOURNAL* I gave a résumé of tests applied in standardizing Digestive Ferments, with special reference to their peculiarities. A second paper, "Influence of Size and Shape of Bottles upon the Assay of Pepsin," appearing in the *Journal of the American Pharmaceutical Association* (Vol. II, No. 12, December, 1913), deals with the assay of pepsin. Further observations with these sensitive enzymes have shown the following peculiarities with:

#### PANCREATIN

In the first mentioned paper I called attention to the fact that in assaying diastasic ferments for starch hydrolyzing power, the kind of starch used is very important, and that the use of potato starch gives an activity  $1/3$  greater than that given when corn starch is used. I now want to carry this statement further and show that one can use two different samples of the same kind of starch; for instance, two samples of corn starch, and unless the physical properties of the two samples are identical, the results will be of wide variation. Of these physical properties reaction is the most important. The U. S. P. says the starch should be neutral to litmus paper, but as a matter of fact, litmus paper is not sufficiently sensitive. I have found that if the corn starch is slightly acid to cochineal indicator, this acidity slightly accelerates the activity of the enzyme, although litmus paper would show the starch to be neutral, and further, a strength of acid in the starch which would show acid to litmus paper, would inhibit the activity of the diastase.

On the other hand, a slight alkalinity in the starch, shown by cochineal solution, would inhibit the diastasic activity, although here again the alkalinity would be so slight as to cause the starch to appear neutral to litmus paper. The following experiment will illustrate these points:

Starch No	Moisture		Ash	Per cent	Reaction to litmus	Reaction to cochineal	Acid equivalent in HCl abs by wt	Equivalent in Per cent KOH	Activity of same sample of pancreatin shown
	Per cent	Per cent							
1.....	0.66	0.1			Neutral	Slightly acid	0.0023	1	25 in 4 mins
2.....	4.66	0.18			Neutral	Alkaline		0.031	1 : 25 in 10 mins.
3.....	6.66	0.1			Neutral	Neutral			1 : 25 in 4 mins. 15 secs

The table shows that starch No. 1, in which the pancreatin tests 1:25 in 4 mins., has an acidity by cochineal of 0.0023 per cent HCl absolute by weight, although it

<sup>1</sup> Presented at the 47th Meeting of the A. C. S., Milwaukee, March 25-28, 1913.



seems neutral to litmus paper, and if this acidity be carefully neutralized, the diastase requires 15 seconds more to hydrolyze the starch and if now the starch be made to have an alkalinity equivalent to 0.031 per cent KOH, the activity of the pancreatin changes from 1 : 25 in 4 mins. to 1 : 25 in 7 $\frac{1}{2}$  mins., although the starch still meets the U. S. P. requirements and is neutral to litmus paper.

It would therefore appear to one unaccustomed to working with these enzymes that the pancreatin had lost some of its diastasic activity, when the real truth of the matter is that the presence of the slight alkalinity in the starch inhibited the starch hydrolyzing power of the diastase.

The percentage moisture in the corn starch on the market varies, but a difference of 2 per cent more or less is not an important factor, as the following figures show.

If the diastase tests 1 : 25 in 5 minutes on starch of 4.66 per cent moisture, it tests 1 : 25.5 in 5 minutes on starch of 6.66 per cent moisture, or 1 : 25 in 4 minutes 54 seconds: *i. e.*, 2 per cent more moisture in the starch, or what is the same thing, 2 per cent less starch, showed the diastase to have an acceleration of but 6 seconds. However, a difference in moisture content as great as 10 per cent would show a decided effect upon the final strength of the diastase, but the average samples of starch would not vary to such an extent.

It is my custom, before adopting a sample of starch for diastasic assay, to wash it thoroughly with 10 times its volume of distilled water and after drying to determine its moisture and ash content, then to shake it up with neutral, recently boiled and cooled, distilled water, and after filtering to test the filtrate with cochineal indicator, and to make use of the starch only when it shows neutral to this indicator. As a further check, I test a known sample of pancreatin with it.

A third precaution to eliminate variations in assay, is to use always a diluted iodine solution of the same temperature. A warm iodine solution does not show the starch iodide reaction so readily as a cold one.

These three precautions then should always be observed if uniform results are to be obtained:

I—The starch should be neutral or at most but very weakly acid.

II—It should be chosen of average moisture content with a preference toward the use of anhydrous starch.

III—The temperature of the diluted iodine solution should be constant.

DIGESTIVE FERMENTS COMPANY  
DETROIT

## LABORATORY STUDIES ON MALT EXTRACT<sup>1</sup>

By HOWARD T. GRABER

Some years ago I started an investigation upon the concentrated glycerine extracts of malt to determine the nature of the changes which take place in malt extract upon aging and the causes of said changes. I was not successful in assigning any specific composition change and therefore did not submit my results

for publication. However, as there may be some points of interest in the work done, the results are published herewith.

For many years it has been known that malt extracts, of the concentrated glycerin variety, assume a dark color very soon after manufacture, and upon aging a year or more acquire an acid taste and an odor of decomposition.

The questions have been: (1) Does this change affect the diastasic power of the extract? (2) Is this change brought about by any characteristic change in the composition of the extract?

To answer the first question, samples of malt extract, the diastasic power of which had been determined at the date of manufacture, were carefully selected from a series extending back twelve months and their starch hydrolyzing power again determined.

Five grams of the extract were diluted to 100 cc. with distilled water and thoroughly mixed: 10 cc. of this dilution were then added to 100 cc. of a 2 per cent starch paste of 40° C. and the mixture maintained at 40° C. until hydrolysis was complete, noting the time required to completely digest the starch; the point of complete hydrolysis being taken at that time when one drop of the digested starch liquor failed to produce the slightest trace of color when added to 50 cc. of a solution containing 0.0006 g. of iodine and 0.0012 g. of potassium iodide. The results follow:

Original assay at date of manufacture	Second assay Minutes	Age of extract	Original assay at date of manufacture	Second assay Minutes	Age of extract
7	7	12 months	9	9	6 months, 21 days
9	15	12 months	9	9	6 months, 14 days
7	13	10 months, 15 days	7	7	6 months, 7 days
10	10	10 months	7	7	6 months, 3 days
10	10	10 months	8	8	6 months
14	14	9 months	8	8	5 months, 20 days
7	7	7 months, 20 days	8	8	5 months, 14 days
8	8	7 months, 13 days	9	8	4 months
9	9	7 months, 5 days	7	7	3 months

All of the above extracts were very dark in color and most of them had developed a disagreeable odor. It is evident that the change which had taken place had not affected the diastasic, and therefore, the medicinal properties of the extracts.

The second question is not such a simple one. The extractive matter dissolved from malted barley by means of water and glycerin, consists of albumenoids, phosphates, maltose and dextrose, dextrin, and a peculiar principle termed diastase, as well as asparagine and carbohydrates of a higher rotary power called "malto-dextrine." To form any conclusions as to the nature of the changes taking place, most, if not all, of these ingredients should be determined. For this work I selected samples ranging in age from several weeks to three years.

The theory of the method used was: (1) To exhaust the malt extract with absolute alcohol. From this alcoholic extract the percentage of maltose and dextrose as well as other data were obtained. (2) The

<sup>1</sup> Presented at the 47th meeting of the A. C. S., Milwaukee, March 25-28, 1913.

residue from the alcoholic extract after careful drying was exhausted with distilled water and from this water extract the percentage of dextrins and albumenoids was obtained.

The apparatus used consisted of the usual Soxhlet extractor, with bulb condenser, cellulose filter about 4 inches long, sand which had been previously washed with hydrochloric acid and subsequently freed of acid, and absolute alcohol which had stood over unslaked lime while boiling 24 hours in a reflux condenser and distilled immediately before use.

Into the cellulose filter introduce about 30 grams of the dried sand: filter and sand were carefully tared upon an analytical balance and upon the sand 10 grams of the malt extract were accurately weighed. The filter with its contents was then placed in the extractor and this was in turn connected at its upper end with a bulb condenser and at its lower end with a 16 ounce distilling flask by tightly fitting rubber stoppers covered with tinfoil. The 16 ounce distilling flask contained about 10 ounces of recently redistilled absolute alcohol, and was shielded from the direct flame of a Bunsen burner by a sand bath.

The extraction of the malt extract by the absolute alcohol was continued for about 48 hours at intermittent intervals of 8 hours at a time, or until a portion of the alcohol siphoning from the malt extract failed to reduce Fehling's solution, showing that all the sugars had been extracted, and also left no weighable residue upon evaporation.

means of DeFrens' table given in Leach's "Food and Drug Inspection," pages 595 to 597. This finished the work on the alcoholic extract.

The apparatus consisting of the cellulose filter, sand, balance of the malt extract, together with the distilling flask were carefully dried; and, after drying were connected up as before, using the same quantity of distilled water as of absolute alcohol in the previous extraction.

The distillation was continued for another 48 hours at 8-hour intervals or until a portion of the water siphoning from the filter did not leave a weighable residue upon evaporation.

This constituted the second or aqueous extract. It was made up to 500 cc., thoroughly mixed and from it the following determinations were made:

1—Total solids and

2—The percentage of dextrin and albumenoids.

The total solids were obtained as in the alcoholic extract. The percentage of dextrins and albumenoids was calculated as the difference between the total solids and the per cent of ash. The other determinations made were moisture, acidity and diastasic strength.

The acidity was determined by diluting 2 grams of the original extract to 250 cc. with distilled water and titrating with  $N/10$  sodium hydroxide using phenolphthalein as indicator direct, or if the solution was too dark the dropping plate was used, and the acid calculated to lactic acid. The results follow.

Age of malt extract Months.	ALCOHOLIC EXTRACT				AQUEOUS EXTRACT				Ash	Total determined cal- culating from total solids	Total determined cal- culating from sugar	Undetermined cal- culated as albumenoids and diastase	Diastasic strength when manufactured Min	Present diastasic strength Min	Lactic acid Per cent
	Soluble in al- cohol	In- soluble in water	Per cent	Total solids	Maltose and dextrose	Total solids	Per cent dex- trin	Moisture							
33	1.82	60.51	58.85	9.3	8.42	29.26	0.88	101.77	99.23	0.77	10	45	4.5		
30	0.57	53.66	52.01	13.3	12.7	31.04	2.04	100.61	98.36	1.64	10	45	4.26		
24	1.84	55.68	50.27	8.86	7.19	32.34	1.67	100.39	93.25	6.73	6	9			
23	0.65	52.53	49.64	15.34	13.50	33.37	1.84	103.73	99.00	1.00	6	10			
17	1.16	57.50	53.36	12.37	10.87	29.16	1.5	101.69	96.05	3.95	8	13			
8	0.71	55.82	53.54	6.25	4.52	36.00	1.73	100.51	96.50	3.50	9	9			
1	0.65	59.96	52.62	11.11	9.06	30.47	2.05	104.24	94.85	5.15	6	6	0.09		

This alcoholic extract contains all of the sugars, some coloring matters with resins from the hops and some glycerin. It was evaporated to dryness at 80° C., the residue dissolved in distilled water and the solution made up to 500 cc. with distilled water and filtered upon counterpoised filter papers.

From this solution the following determinations were made:

1—The percentage of extract soluble in alcohol but insoluble in water. This was determined by drying and weighing the contents of the filter paper above.

2—The percentage of total solids in the portion soluble in alcohol and soluble in water. This was determined by weighing 20 cc. of the solution in a tared dish, evaporating to dryness and weighing again.

3—The percentage of reducing sugars was determined gravimetrically by means of Fehling's solution, calculating the weight of reduced CuO to maltose by

## CONCLUSIONS

I—Malt extract even after having changed to an almost black color and having a disagreeable taste is not necessarily inactive, and when properly made it is potent for at least one year.

II—Although the analysis of the extracts of different age did not show any definite series of changes in sugar or dextrin content, no definite conclusions could be drawn as to just what the nature of change was which took place. The results do indicate what the cause might be and further experiments have convinced me that the cause of the deterioration of the diastasic power of malt extract is due to the development of lactic acid and when the amount reaches a strength of 1 per cent or more it greatly impedes starch hydrolysis. This developed acidity also undoubtedly causes the above mentioned blackening of the extract.

DIGESTIVE FERMENTS COMPANY  
DETROIT

## LABORATORY AND PLANT

### THE PYROMETER IN THE ASSAY MUFFLE<sup>1</sup>

By FREDERIC P. DEWEY<sup>2</sup>

Standing alone, by itself, a pyrometer reading has absolutely no value as a control of assay operations in a muffle or as a guide to the assayer in carrying on such operations. The reasons for this are varied and complex. (1) The temperature that controls the success of the operation is that of the lead button undergoing oxidation. At present we have no means of learning this temperature under practical working conditions, so that some suitable place must be selected within the muffle for the location of a pyrometer. (2) Unfortunately, however, there is absolutely no approach even to a fixed relation between the pyrometer reading at any given point available and the temperature of the oxidizing button. The oxidation of the lead supplies much heat to the button, but its effect upon the pyrometer is negligible. One factor governing the amount of heat utilized by the button is the rate of oxidation of the lead, and this in turn is, within wide limits, largely influenced by the passage of the air over the button, so that to fully utilize and apply the pyrometer reading we must also know the height of the barometer and the effect of variations in the barometer readings upon the draft of the particular muffle under consideration. Further and most important, from a practical standpoint, is the freedom of entrance for the air to the muffle. In other words, by manipulating the door or the stopper of the muffle, widely varying differences between the button temperature and the pyrometer reading may be produced. The effect of the door conditions is twofold. It affects the supply of air to the button and also the actual temperature of the bottoms of the muffle on account of the varying amounts of air that have to be heated there in passing through the furnace. Finally the relation of the position of the button within the muffle to that of the pyrometer is vital. Therefore, to intelligently utilize any stated pyrometer reading it is essential to have exact information upon a variety of other conditions surrounding the operation.

Bradford<sup>3</sup> pointed out the inconsistencies of various statements regarding pyrometer readings in assaying and well established facts, such for instance as advising a temperature of 700° to 750° for cupellation when it requires at least 906° to fuse litharge. In a series of tests he demonstrated the large amount of heat supplied by the oxidation of the lead and the higher temperature thereby attained by the button. His arrangement of apparatus was ingenious, but risky to the pyrometer couple and not applicable to routine work. He gives an excellent description of the conditions immediately surrounding a cupellation.

Fulton, Anderson, Goodner and Ossa<sup>4</sup> determined

<sup>1</sup> Presented at the 49th Meeting of the A. C. S., Cincinnati, April 7-10, 1914 and published by permission of the Director of the Mint. Published simultaneously by the American Institute of Mining Engineers.

<sup>2</sup> Assayer, Bureau of the Mint.

<sup>3</sup> *This Journal*, 1, 181.

<sup>4</sup> *West. Chem. Met.*, 4, 31.

the difference in temperature between an empty cupel and the cupelling lead in an adjoining cupel as 145°, and also give various other temperature determinations, under the conditions employed by them.

For a long time I have been engaged upon an investigation into the conditions surrounding the assay of gold bullion as affecting the accuracy of the results obtained. Naturally the question of the temperature of cupellation early attracted attention, but there were so many other conditions to be investigated where our information was meagre, while the temperature question seemed to be under fairly good control by the eye of experienced cupellers, that the use of the pyrometer was not actively taken up until recently.

In the early days of the investigation various points regarding temperature were carefully considered and some of the problems were worked out. Some of the problems presented themselves with emphasis. In this connection a careful distinction should be drawn between the problem of ascertaining the effect of the various conditions of the cupellation upon the temperature of the cupelling bead and the problem of the regulation and adjustment of these conditions so as to produce the best possible conditions for cupelling, and the final problem of establishing a suitable indicator or guide to show that the proper conditions are being maintained, and especially an indicator which may be applied in different muffles and under varying conditions.

In a broad and general way the time required to work off a given weight of lead is a crude indication of the temperature of the cupellation. When carrying on uniform work in quantity the decreasing size of the button is a general guide for the temperature and a rough notation of the time will often be useful in explaining irregularities of the results. If the general conditions remain uniform, a prolonged cupellation indicates lack of heat, and a rapid one an excess of heat. In making time observations it is essential to adopt some fixed point in the operations to begin taking the time and another to stop. If all the other conditions could be rigidly controlled and the time be very carefully observed, it would furnish a good guide to the temperature, but it would be available only at the finish of the run and could not be used to change conditions during the run. Also, it could not be applied at other times or places or under different conditions. Again it furnishes no preliminary evidence that the furnace is in good condition before starting the work.

It is, however, hardly ever possible to control the other conditions and sometimes accidental variations creep in. On one occasion, when the conditions, including the temperature, appeared to be normal, it became evident that the lead was not oxidizing fast enough. An examination showed that in setting a new muffle the workman had not put the slit in the back of the muffle exactly opposite the chimney outlet. This choked off the draft and retarded the oxidation. The retardation of the work was, of course, excessive, but



this experience emphasizes the natural effect of changes in the barometer upon cupellation. A resetting of the muffle corrected the difficulty.

Another *post facto* temperature indicator is the amount of gold absorbed by the cupel in gold bullion assaying, high absorption under similar conditions, indicating high temperature. Here again controlling the other conditions is difficult and I have found this indicator to be of value largely in emphasizing the fact that variations in the other conditions may falsify the pyrometer reading. It makes a difference whether the pyrometer is rising or falling. If we could hold the pyrometer at the same point for a long time before making the cupellation this cause of difference would be minimized, but this is impracticable in every-day work. It makes a difference if the muffle be new and in good condition or old and nearly worn out, and it must not be forgotten that a new muffle may be poor and leak more than an old one, which was of good quality when new.

The only feasible place to put a pyrometer in an assay muffle is close to the top of the arch of the muffle and for convenience it must be inserted from the back. We all know, of course, that closing the muffle increases the temperature and that on moving toward the back of the muffle the temperature rises, as practical every-day working facts. In order to get a more exact idea as to the difference in the temperature in different parts of the muffle and the relations between these temperatures and the fixed pyrometer readings, a second portable pyrometer was placed on the bottom of the muffle in varying relations to the fixed pyrometer as follows: directly under the fixed pyrometer, at the right side and at the left side in the same cross-section as the fixed pyrometer, close to the front in the middle and on each side of the muffle. In some of the arrangements empty cupels were placed beside the bottom pyrometer.

There are three principal causes for differences in the two pyrometer readings: position within the muffle, freedom of entrance of air to the muffle, and condition of the burners on either side of the muffle. In general, the door conditions, governing the entrance of air to the furnace, exert a powerful influence upon the temperature within the muffle, and often cause wide differences in temperature in different parts of the muffle. Under the conditions of these tests, on opening the closed muffle, either pyrometer may fall 100° or more in ten minutes, and a further 10° or 20° before becoming steady. In the closed muffle the two pyrometers registered alike in only one instance, and differed 40° in one. In every instance the movable pyrometer, on the bottom of the muffle, fell more than the fixed pyrometer, at the top of the arch, on opening the closed muffle, and in one instance 40° more.

A point of grave concern is the stability of the pyrometer. In the above tests both of the pyrometers were practically new and may be depended upon, but the effect of long use, for continuous periods, in the litharge-laden atmosphere of the muffle upon the instrument is unknown. It is known that the hot litharge fume is destructive to the tube, and it is only a question of time when it will affect the enclosed couple. At present there are no ready means for testing the accuracy of the pyrometer from time to time, and

it is difficult for an assayer to judge when it is beginning to fail.

In conclusion, I would say that, notwithstanding the objections I have described, the pyrometer occupies a useful field as a general guide to the heat conditions in the assay muffle. In the old and established practice of assaying in the Mint service, in the large laboratories, one or two men do practically all of the cupelling and they grow to be very expert in judging the heat of the muffle and the condition of the cupelling bead by the eye, but the careful and proper use of a pyrometer would often help them, while the man who cupels only intermittently will find it a good general aid. But too much dependence must not be placed upon the pyrometer, and the man who depends upon it entirely will never be a good cupeller.

BUREAU OF THE MINT  
TREASURY DEPARTMENT, WASHINGTON

#### APPROVED BUREAU OF MINES EXPERIMENT STATION AT PITTSBURGH

Plans for the proposed \$500,000 Experiment Station of the United States Bureau of Mines to be located in Pittsburgh, have been approved by the commission appointed by Congress for that purpose.

Congress, a year ago, in the Public Buildings Bill, authorized a new home for the Bureau of Mines to cost \$500,000. It is now expected that Congress, in its present session, will make a specific appropriation so that construction work may begin. It is hoped that contracts may be let by July 1st and the buildings completed in the fall of 1915.

The State of Pennsylvania has appropriated \$25,000 for coöperation in establishing this Experiment Station.

The group consists of three main buildings facing Forbes Street. The central building of the group, the Mining Building, will be three stories in height, flanked by two main buildings, one the Mechanical and the other the Chemical Building. In the rear of these and enclosing a court will be the Service Building. Beyond the Service Building and spanning what is known as Panther Hollow and thus connecting the Bureau of Mines Buildings with the Carnegie Schools, will be two buildings over the roofs of which will pass the roadway from Forbes Street to the Carnegie School Buildings and Schenley Park.

Between the main group and the power and fuel group will be the entrance to a series of mine shafts. One of these will be used as an elevator to carry heavy material and passengers from the lower level to the upper; another will be for tests of hoisting ropes and similar mining appliances; another will be an entrance to tunnels extending under the buildings and in which mining experiments, such as fighting mine fires, will be conducted.

The portion of Panther Hollow above the Power Buildings will be arranged as a Miners' Field, the slopes of the ravine being utilized as an amphitheatre which will accommodate 20,000 spectators who may assemble here to witness demonstrations and tests in mine rescue and first-aid.

The Mining Building will contain the administrative offices, and those of the mining force. In it will be



APPROVED BUREAU OF MINES EXPERIMENT STATION AT PITTSBURGH

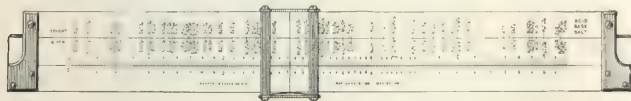
an assembly and lecture hall, a library and smoke and other rooms for demonstrations and training in mine rescue and first-aid. The Mechanical Building will be for experiments and tests of mining machinery and appliances and the Chemical building for investigation and analyses of fuels, explosives and various mineral substances.

### THE CHEMIST'S DUPLEX SLIDE RULE

By H. H. HANSON

Received February 12, 1914

In these days of efficiency and specialization, any contrivance or device which tends to save time without sacrifice of accuracy is eagerly seized upon. The slide rule has long been used by engineers. It is only within



recent years, however, that its use has been applied to chemical problems. There have been placed upon the market several so-called "Chemist's Slide Rules," but the "Duplex," invented by Dr. R. Harmon Ashley, of the University of Maine, and manufactured by the Keuffel & Esser Co., of New York, seems to be a material advance over previous rules of this kind. This rule has both the regular and the inverted scales, with the graduation incident to instruments of this kind, so that in itself it is complete, and upon it may be carried out all of the arithmetical computations which are usually required of a chemist or chemical engineer. In addition to this it carries one hundred and thirty-five chemical symbols, the acids, bases and salts being on the regular side, and oxides and elements

being on the inverted side. The left index of the rule is marked "Sought," the left index of the slide is marked "Given," so that no mistake can be made in the setting it be used. With the large number of chemical symbols given almost any stoichiometric problem may be solved, as hundreds of combinations are possible with the instrument. Conversion factors are very easily and quickly obtained with one setting of the rule. The percentage composition of various compounds may be found, and problems in both gravimetric and volumetric analysis may be easily solved as described in the manual which accompanies the rule. The molecular weights of substances not inscribed on the rule are easily obtained, even though the compounds may not be given, as forty-two different elements are inscribed upon the invert side. The illustrations show the general appearance and plan of the instrument, which is very finely made and accurately marked. The gradua-

tions and symbols are inserted mechanically, thus eliminating the errors necessarily accompanying hand markings of this kind. This rule is accurate to three significant figures within a limit of error which does not exceed that of the average operation of the analytical chemist, and will be found useful for shortening operations and calculations in all branches of chemical



work. In the manual accompanying the instrument the theory of the slide rule is briefly and carefully explained, and the manner of operation is described in detail.

MAINE AGRICULTURAL EXPERIMENT STATION, ORONO

## ADDRESSES

### THE CHEMISTS' CLUB<sup>1</sup>

By WILLIAM L. DUDLEY

Almost all the professions in the United States have, in addition to their scientific associations and societies, an organization whose purpose is to foster and develop personal and professional acquaintance among the membership of that profession in a direction and to an extent not possible in strictly scientific associations. The scientific associations are not

adapted to bring about this result to the greatest degree, primarily for the reason that between their meetings there is no opportunity for individuals to meet; the opportunities afforded by such scientific associations for personal intercourse are therefore intermittent and discontinuous. Continuous opportunity for such acquaintance and intercourse is offered only by those professional associations known, for short, as "clubs," which have club features as a basis, associated or combined with professional facilities and opportunities peculiar to each profession. These two classes of organizations are therefore mutually

<sup>1</sup> Presented at the Cincinnati Meeting of the American Chemical Society, April 6-10, 1914

complementary and helpful and are not in any conflict with each other.

Up to three years ago, the chemical profession in the United States was not equipped with any association or organization having the continuous club feature as an element. It is true



ENTRANCE HALL

that prior to that time The Chemists' Club, founded in 1898, with its quarters at 108 West 55th St., New York City, discharged to a greater or less extent the functions of a club, but in a manner not sufficiently continuous to meet in any satisfactory degree the needs of the chemical profession of the United States.

It was through the energy, devotion and self-sacrifice of a number of far-sighted, broad-minded and public-spirited chemists that the chemical profession, about three years ago, became possessed of quarters which contain all the elements necessary for continuous opportunity of social and professional intercourse among chemists under conditions of the usual club accommodations connected with unique and complete facilities for the conduct of professional business of all kinds under one and the same roof. To those who are engaged in the practice of industrial chemistry, such an opportunity means much. A chemist with his laboratory is not welcome as a tenant in modern high class, centrally located and well equipped buildings, and, as a result, in most of the cities, and particularly in New York, the chemist and his laboratory are crowded into the less desirable sections of the city, and then only in the less desirable buildings.

When the chemists desire to hold a meeting, they generally do so in rented quarters, poorly equipped for demonstration and experimental purposes. If a chemist desires access to chemical literature, he will find in only isolated cases a suitable library, and in still rarer instances will he find such library in charge of one who has an understanding of what chemical literature is, and what a chemist's literary needs are. If a manufacturer desires to engage a chemist for a piece of work requiring particular experience, he has, apart from The Chemists' Club, practically only the colleges and universities as a source of supply. If a chemist desires a position, he is in most cases limited to the same source of information.

The new quarters of The Chemists' Club constitute the only place in the world where chemists, above all others, are welcome, are sought as tenants and have laboratory and library facilities, under one and the same roof; where competent attendants provide them with literature, keep them informed of current events in their individual specialties, provide them with temporary laboratories, with apparatus and with chemicals, and enable them to engage help such as they may need. At the same time, they have, under the same roof, all the accommodations of a hotel, with the particular homelike features of a club, where they can always meet men of their own training and of their own line of thought; in short, once installed at The Chemists' Club, there is hardly any need of their leaving the building for anything that they might want in the way of professional or laboratory facilities, for social intercourse, for shelter or for food.

The Chemists' Club, although it is a New York corporation, and although it is located in New York City, aims to serve all the chemists and chemical industries of the entire United States, and for that purpose it has divided its membership into resident and non-resident. It is perfectly obvious what the resident members can get out of The Chemists' Club, and that what they can get is greater than what non-residents ordinarily would get, and that is why the resident member must pay larger annual dues than the non-resident.

It is clear, however, that an organization based upon national lines and doing work of a national scope must have more than local support, and in order to accomplish the greatest good must receive the widest possible support from those living outside of the resident membership area. When a non-resident member goes to New York, he can have, during his stay, all the advantages that a resident member can enjoy, and it is perfectly clear that those chemists resident outside of New York



SOCIAL ROOM

City, and who make even only occasional trips to New York, would be greatly benefited by acquiring non-resident membership and availing themselves of the Club facilities and opportunities when in New York City. Such members may very well want to have a temporary laboratory about which they can



throw all the privacy of their own laboratory. The Chemists' Club is prepared to supply this need, a service not offered by any other professional organization in the world.

As to non-resident members who never reach New York, the advantages and benefits of The Chemists' Club are perhaps

Those members of the chemical profession, and all engaged in industrial pursuits dependent upon chemists or in which the chemist plays a part, owe it to themselves and to the future of their own profession or business to see to it that opportunity for growth and development is as great as possible. The Chemists' Club offers the best opportunity for such growth and development, and it cannot reach its highest state of efficiency until every public-spirited and high-minded member of the chemical profession or industry has contributed his share to



CHANDLER LIBRARY

not quite so obvious, but nevertheless valuable and certain; some day these non-resident members will want to have literature compiled or translated for them in a hurry, and at no place can it be done as well as at The Chemists' Club; or they may wish to have information as to the literature of a certain art, and that can be done no better anywhere than at The Chemists' Club; they may want to have in their hands a book not accessible at their local libraries; if such book is in duplicate in The Chemists' Club library, it is loaned to them, and if not in duplicate, a copy, photographic or otherwise, will be made and forwarded at a substantial cost; or they may want to obtain the services of a man skilled in a particular branch—the only place that they can turn to and get satisfactory information is The Chemists' Club. It may very well be that a particular non-resident member might want such service only once in two years, but if he does, whatever he has expended in the way of membership fees is undoubtedly amply repaid by the very fact that such opportunities exist and are always at his command. Preparedness and ability to do, or have done, such things is something of such great value, that beside it the annual contribution towards the realization and maintenance of such a state of affairs is wholly insignificant; each chemist must make his contribution so that these opportunities may exist when he needs them. It is merely another variation of "In time of peace prepare for war."

Coöperation is the only way in which a profession can advance, and the opportunity of coöperation necessary to the advancement of the chemical profession is offered by The Chemists' Club. Without personal contact with men of the same profession and without opportunity for such professional contact, the growth of the profession must necessarily be slow, if it does not diminish to an extent properly to be described as a standstill.

THE MEMBERSHIP OF THE CHEMISTS' CLUB

Year	Resident, life and honorary	Non-resi- dent and foreign	Junior	Total
1898	41	48	..	89
1899	135	56	..	191
1900	130	109	..	239
1901	143	118	..	261
1902	138	123	..	261
1903	150	134	..	284
1904	172	142	7	321
1905	164	166	11	341
1906	169	165	22	356
1907	195	161	25	381
1908	208	167	24	399
1909	225	167	19	411
1910	308	341	28	677
1911	412	524	47	985
1912	447	570	75	1092
1913	447	607	80	1134
1914	455	638	92	1185

the extent, at least, of becoming a non-resident member, and making full use of the opportunities offered.

An organization like The Chemists' Club grows with the service required of it, and with the support given it; it is to be hoped that every chemist wherever he may reside in the United States, and every person engaged in business involving chemistry, will feel that he has not done his full duty by the profession and business of chemistry until he has actively identified himself in some way or other with The Chemists' Club.

It is now three years since the new quarters at 50-52 East 41st Street, New York City, were opened, and those who have



DINING ROOM

sacrificed much time and effort in developing The Chemists' Club to its present state feel encouraged by the growth in the interest in the Club which is manifested throughout the United States.

In order that a mental picture of the growth of The Chemists' Club and its influence may be obtained, information has been collected as per table on preceding page.

#### LABORATORIES

Of these there are five floors and all of them rented to permanent tenants. The three "transient" or so-called "Club" laboratories, which are maintained by The Chemists' Club, have all been taken and usually there is a waiting list of satisfactory size.

#### LIBRARY, CLERICAL, LINGUISTIC AND LITERARY SERVICES

The library now contains 36,000 volumes, including 400 journal sets. Many of the volumes (18,000) are duplicates or triplicates and are available to members for loan purposes for which no charge is made except that necessary (25 cents) to cover cost of packing and insurance, the member paying transportation charges both ways.

The range of service rendered by the library staff includes

The clerical, linguistic and literary service was begun in March, 1913, and the following statistics show a satisfactory and wholesome growth in the work:

	Translations		Subscribers to the clipping service	Searches, literary and patent
	No.	No. of words		
1913				
March	2	2,850	4	1
April	3	8,010	6	6
May	3	37,506	8	10
June	6	9,540	21	14
July	9	15,030	22	7
August	8	1,325	24	7
September	17	25,300	28	10
October	14	25,525	30	10
November	9	90,800	48	7
December	11	36,940	51	11
1914				
January	14	26,525	55	18
February	28	62,675	58	19
Total	121	342,020	—	120

The translations average 2,826 words each and 26,300 words per month, or 10 average translations per month. These services, *i. e.*, translations, clippings, searches and copies or photographs as well as the use of the library are available to the public and are not restricted to the membership of The Chemists' Club.

#### EMPLOYMENT BUREAU

This was begun in 1905. Its activities are reflected below; its use is open to all, whether members of The Chemists' Club or not:

	APPLICANTS		POSITIONS	
	Enrolled	Placed	Enrolled	Filled
1905	60	21	28	21
1906	80	20	51	20
1907	351	86	108	86
1908	582	39	64	39
1909	220	72	120	72
1910	245	92	217	92
1911				
1912	464	170	216	120
1913	647	119	294	119
1914 - January and February	112	15	66	15
Total	2761	584	1164	584

A total of 584 positions was filled in 8 years (omitting 1911 for which figures are not available), or an average of 73 positions per year; the disparity between positions available and positions wanted, namely 2 to 5, or in numbers 1597, clearly shows the desirability of encouraging employers of chemists and of chemical assistants to make more extended use of this branch of The Chemists' Club.

#### RESTAURANT

In January, 1912, The Chemists' Club took over the management of the restaurant from the caterer, who had theretofore conducted it. The number of meals served for each month since is as follows:

	1912	1913	1914
January	901	1,482	1,898
February	1,162	1,522	2,245
March	1,577	2,051	..
April	1,643	1,924	..
May	1,483	1,631	..
June	1,392	1,488	..
July	1,352	1,540	..
August	1,599	1,320	..
September	3,930	1,328	..
October	1,392	1,503	..
November	1,409	1,462	..
December	1,495	1,600	..
Total	19,335	18,851	..
Monthly average	1,611	1,571	2,070

Many times the patronage that has so far been bestowed upon the restaurant could be satisfactorily served, without in the slightest crowding or overworking the mechanical equipment of the restaurant (which is the smallest unit that could be installed).



ENTRANCE TO AUDITORIUM

not only copies or photographs of publications or of pages thereof and translations into English from other languages, but also the collection of the literature in not only the library of The Chemists' Club but other libraries in New York City or elsewhere, if necessary; further, systematic recording of current literature in which members may be professionally and otherwise interested and for which they pay a nominal fee; searches

#### USERS OF THE CHEMISTS' CLUB LIBRARY

	1911	1912	1913	1914
January	124	148	346	..
February	137	190	348	..
March	127	196	..	..
April	129	224	..	..
May	133	252	..	..
June	151	257	..	..
July	77	150	227	..
August	75	131	260	..
September	98	134	256	..
October	109	125	261	..
November	106	105	230	..
December	115	100	330	..
Average	95	129	238	347

of literature, patent and otherwise, on intricate and complex chemical questions as well as statistical and similar searches and compilations are undertaken.

The number of users of the library is increasing as shown in the preceding table.

## SLEEPING ROOMS

The information regarding these shows clearly how our non-resident membership is increasing its use of the quarters provided; the tenancy of these 18 rooms is divided into resident members and non-resident members and guests; the number of times per month that the quarters were all taken, *i. e.*, "sold out" and that members had to be sent to the "Annex" (The Murray Hill Hotel) for the night is shown in the following:

	Resident		Non-resident		Guests		Total		"Sold out"	
	1912	1913	1912	1913	1912	1913	1912	1913	1912	1913
January.....	9	22	45	53	12	11	66	86	0	3
February.....	13	15	55	41	10	3	78	59	1	1
March.....	14	14	49	47	9	4	72	65	0	1
April.....	15	16	37	48	11	5	63	69	4	5
May.....	17	17	47	47	2	12	76	76	1	4
June.....	21	14	37	47	8	10	66	71	11	5
July.....	21	17	37	46	8	13	66	76	8	8
August.....	21	19	28	32	2	9	51	60	1	8
September.....	14	17	37	45	4	5	55	67	7	3
October.....	17	19	40	49	10	4	67	72	1	7
November.....	18	18	36	45	7	6	61	69	1	2
December.....	15	21	40	60	9	7	64	88	0	4
1914										
January.....	16		62		15		93		8	
February.....	16		53		8		77		4	

However, even with this encouraging showing, it is nevertheless true that The Chemists' Club itself can provide hotel accommodations to very many more than are now making use of it.

## SOCIAL GATHERINGS

From January 11, 1912, to March 1, 1914, 111 private dinners or public banquets and all connected with meetings of a chemical nature were given in the quarters of The Chemists' Club; these were attended by 6539 persons.

## RUMFORD HALL

This is an auditorium seating 300; is equipped with ample demonstration and experimental facilities. It is the regular meeting place of the New York Sections of The American Chemical Society, The Society of Chemical Industry and The American Electrochemical Society.

A number of social, musical and literary organizations not connected with The Chemists' Club also use Rumford Hall for their several functions.

This showing demonstrates a healthy growth in the membership of and in the interest in The Chemists' Club since it left its modest quarters at Fifty-fifth Street, where it provided merely a meeting place for the New York Sections of The American Chemical Society, The Society of Chemical Industry, The American Electrochemical Society and The Verein Deutscher Chemiker; there it had its own modest library, combined with the libraries of the American Chemical Society and the Society of Chemical Industry.

The new quarters and the new facilities are due to the initiative, the foresight, the loyal enthusiasm and abiding faith in the ultimate outcome of an enlarged Chemists' Club, on the part of its former president, the late Professor Morris Loeb. By founding The Chemists' Building Company, whose sole aim and object was to finance, build and develop a structure suitable for what was then considered as the true and full purpose of The Chemists' Club, the start was made toward an actual realization of what had long been in the mind's eye of many of the thoughtful and far-seeing chemists of the country, as a true and real and serviceable Chemists' Club.

The Chemists' Building, which is the home of The Chemists' Club, is an eleven story fire-proof structure, centrally located in New York City and having a 56-foot frontage. The structure put up and the facilities provided are on the smallest scale that could reasonably be regarded as being efficient. Nevertheless, the total investment of The Chemists' Building Company in the building occupied to the extent of 50 per cent of its avail-

able renting space by The Chemists' Club is appraised at \$440,000 for taxation purposes. Practically all the stock of The Chemists' Building Company is sold, and fully paid up, and is held wholly by members of the chemical profession and business. The capital stock was taken by 171 subscribers; 139 subscribers domiciled in the resident membership area took seven-eighths of the capital stock and 32 subscribers domiciled in the non-resident membership took the remaining one-eighth.

Some of the stockholders, following the example of the late Professor Loeb, have cancelled their stock, or transferred it to The Chemists' Club. The issued stock calls for a cumulative 3 per cent dividend; no dividend has yet been paid nor are the stockholders insisting upon such payment. This magnanimous and generous action on the part of the stockholders is bringing nearer and nearer the day of a complete realization of what was planned by the Founders of The Chemists' Building Company and it is confidently expected that these dividend obligations, for which The Chemists' Club is in the final analysis wholly responsible, will be ultimately fully discharged.

The Club itself represents an investment over \$60,000 in library and equipment, thus bringing the total financial investment in this enterprise up to more than \$500,000.

However gratifying the growth shown in the foregoing may be to those who have given the best of their efforts, time and thought to the realization of The Chemists' Club, yet it is perfectly clear that the members of the chemical profession generally have not made a contribution toward the continuance and maintenance of The Chemists' Club commensurate with the benefits derived or to be derived from it, nor can it be truthfully said to be even proportional to the effort and energy contributed towards it by the Founders of The Chemists' Building Company.

VANDERBILT UNIVERSITY  
NASHVILLE, TENNESSEE

## CHEMICAL ABSTRACTING

By JOHN J. MILLER

Received March 19, 1914

At various times and places during the last few years the question of international cooperation in chemical abstracting has been promulgated and has brought forth some comment. So far as we know, however, no comprehensive data concerning this subject have been gathered other than those recently published in *Scienza Gazeta*, the official organ of the International Esperanto Scientific Association. The appearance therein of an article giving the membership of the German, French, London and American societies, the costs of the abstract journals per member, pages of abstracts, etc., prompted an investigation of the figures given and finally the writing of this article.

Table I gives the data (for 1911) printed in the above mentioned periodical and Table II the results of our calculations:

	No members	Total cost	TABLE I				
			Cost per member	Total No of pages	Total No of abstracts	Pages per abstract	Abstracts from other journals
Chemical Abstracts..	5,603	\$31,557.00	\$5.65	4,741	20,916	0.17	1,542
J. Chem. Soc.....	3,132	13,031.00	4.15	2,586	5,159	0.41	169
Soc. Zentr. Bull. soc. chim. Fr..	3,352	14,706.00	4.40	4,422	9,231	0.39	171
Total.....	13,111	66,453.50		14,040	39,379		1,728

The great discrepancies are due to various errors in Table I. For example, for the *Journal of the Chemical Society* no editorial expense seems to have been considered. For *Chemisches Zentralblatt* the total membership of the German Society is



used instead of the number of subscribers to *Chemisches Zentralblatt*. In our calculations three-fourths of the salaries of the editors of the *Journal of the Chemical Society* have been counted as abstract expense and the same is true of the *Journal of the Society of Chemical Industry*. Less than one-half of the pages of the *Journal of the Chemical Society* is taken up with original communications, so we figure that because of their complete index and the attention of the editors naturally required for abstract work as compared with journal work, three-fourths of the editors' energy and time is given to the abstract part of the periodical. Only one-fourth of the *Journal of the Society of Chemical Industry* is original material, therefore it seems proper to consider three-fourths of the editorial expense as due to work on the abstract section.

Table II portrays a number of interesting facts, among which may be mentioned: (1) *Chemical Abstracts* is the largest (in number of abstracts) chemical abstract journal in the world;

TABLE II

	Sub- scribers	Total cost	Cost per member	Total pages	Cost per page per member	Cost per page	Number of abstracts	Cost per abstract
Chem. Zentr., 1909 II, 1910 I <sup>(a)</sup>	1,542	\$21,027.67	\$13.64	4,364	\$0.003	\$4.87	10,542	\$1.99
J. S. C. I., 1912....	4,198	23,593.80	5.62	971	$\left\{ \begin{array}{l} 0.0057 \div 2 = \\ 0.0028 \end{array} \right.$	$\left\{ \begin{array}{l} 24.30 \div 2 = \\ 12.15 \end{array} \right.$	7,200	3.28
J. C. Soc., 1912....	3,248	16,338.20	5.03	2,648	0.00189	6.17	5,833	2.80
Chem. Ab., 1912....	6,219	32,596.00	5.24	3,544	0.00147	9.197	22,689	1.478
Chem. Ab., 1913....	6,673	37,258.00	5.58	4,096	0.00136	9.09	25,971	1.434

(a) No later figures are available.

(2) it costs less either on a basis of per page per member or per abstract than any other journal. Credit has been given for the fact that the pages of the *Journal of the Society of Chemical Industry* contain a little over twice as much material as those of *Chemical Abstracts*. In the *Scienza Gazeta* article the basis of comparison is the cost per member and in Table II this same comparison is made, but obviously such a basis is not the fairest possible because of the great difference in amounts of material furnished the subscribers of the various journals. Neither do we think the cost per abstract to be the best test of efficiency, because the shortest abstracts will be the cheapest and probably not the most satisfactory. The only comparison that seems worth while is the one based on the cost per page per member and therefore we wish to lay emphasis on the figures given in Column 5 of Table II.

Column 6 indicates that increase in membership means nearly a proportional increase in cost per page if the number of

of articles in all of our 633 journals, the articles abstracted by all of them would exceed ours in number.

In another way a most interesting comparison can be made between four of the abstract journals, namely, *Journal of the Society of Chemical Industry*, *Chemisches Zentralblatt*, *Journal of the Chemical Society* and *Chemical Abstracts*. For example, it may be of importance to know what class of chemical articles is abstracted by *Chemical Abstracts* and omitted by the others.

We regret that it has been impossible to obtain the same data for *Zeitschrift für angewandte Chemie* and *Chemiker Zeitung*, but it would be considerable trouble so to do and perhaps is hardly necessary. Through constant reference to these three journals it has been observed that their abstracts are mainly of articles of an industrial nature. *Chemisches Zentralblatt* and the *Journal of the Chemical Society* confine their work largely to pure science, whereas *Chemical Abstracts* covers both branches of chemistry. But in order to determine whether *Chemisches Zentralblatt* and *Journal of the Chemical Society* are complete even in abstracts of pure chemistry we need only to note the figures in the third and fourth columns of Table IV, in the departments of General and Physical Chemistry, Electrochemistry, Analytical Chemistry, Mineralogical and Geological and Biological Chemistry. As to the reverse of this query, that is to say, is *Chemical Abstracts* missing articles abstracted in these other journals, we would say that such an interrogation is proper and important. The answer is that the abstract part of every issue of the following journals is checked shortly after arrival at this office and that any article (of a chemical nature) which has been overlooked is assigned for abstracting (from the original if possible): *Chemisches Zentralblatt*, *Journal of the Chemical Society*, *Journal of the Society of Chemical Industry*, *Chemiker Zeitung*, *Experiment Station Record*, *Bulletin of Agricultural Intelligence* and *Plant Diseases*, *Neues Jahrbuch* and *Stahl und Eisen*. Other abstract journals are watched by various abstractors so there is little danger of missing an article of value.

The facts so far given are likely to suggest even to the casual observer that much of this abstracting work is a matter of duplication and that some step should be taken to bring about a more economical abstracting system. With this we agree.

TABLE III

	No. of journals abstracted	No. of abstracts, including patents	No. of abstracts, excluding patents
Chem. Zentr.....	161 (1913)	10,862 (1913)	9,948
J. C. Soc.....	140 (1911)	5,833 (1912)	Very few patents
J. S. Chem. Ind.....	151 (1913)	7,200 (1912)	2,400
Z. angew. Chem.....	110 (1913)	5,200 (1913)	3,412
Chem. Ztg.....	.....	13,792 (1913)	9,607
Chemical Abstracts.....	633 (1913)	25,971 (1913)	19,025

pages printed is kept constant, and this is true because of the printing factor; e. g., if we should print 3,000 pages and had 3,500 members our printing and distribution (not counting postage) cost would be \$3.12 per page. On keeping the pages constant and increasing the subscribers to 4,000, 5,000, 6,000, 10,000 our per page costs, according to our recent printing contract, would be respectively, \$3.32, \$3.72, \$4.09, \$5.71.

Table III reveals perhaps more than anything else the completeness with which the field of chemistry is covered by the various abstract journals.

The number of journals in each case is taken from the printed list attached to the index of the year indicated. It is perhaps

TABLE IV

	No. of abstracts in one issue of C. A.	No. not found anywhere in		
		J. S. C. I.	Chem. Zentr.	J. C. Soc.
Apparatus.....	20	18	9	13
Gen. and Phys.....	61	56	12	24
Radioactivity.....	20	20	8	14
Electrochem.....	32	30	27	32
Inorg. Chem.....	19	14	2	4
Analyt. Chem.....	33	20	14	14
Min. and Geol.....	6	5	5	2
Met. and Metallg.....	85	61	60	70
Organic.....	84	73	5	Have nearly all
Biological.....	232	Missed almost all	166	
Biological <sup>(2)</sup> .....	209	..	145	..
Biological <sup>(2)</sup> .....	315	..	..	240
Foods.....	20	19	8	16
Water.....	23	22	16	18
Soils and Fertilizers.....	21	19	8	14
Ferm. and Dist. Liq.....	28	23	6	22
Pharmaceutical.....	26	25	9	23
Acids.....	4	4	3	4
Glass and Ceramics.....	17	16	16	16
Cement.....	20	20	18	20
Fuels.....	31	28	25	27
Petroleum.....	20	18	14	18
Cellulose.....	3	1	1	2
Explosives.....	7	5	3	7
Explosives <sup>(2)</sup> .....	19	..	14	..
Dyes and Textiles.....	15	10	10	14
Pigments, Rubber, etc.....	1	1	1	1
Fats.....	8	..	2	6
Fats <sup>(2)</sup> .....	17	13	..	..
Sugar.....	2	..	2	2
Sugar <sup>(2)</sup> .....	21	10	16	..
Leather.....	2	..	1	2
Leather <sup>(2)</sup> .....	8	..	3	..
Leather <sup>(2)</sup> .....	18	14	..	..

<sup>(2)</sup> In order to obtain representative figures these departments were checked in more than one number of *Chemical Abstracts*.

but before further discussion desire to submit the facts given in Table V.

That there is duplication in abstracting in all of these countries is immediately evident and that this condition is most serious in Germany is also clear. The size, scope and value of the above-mentioned German journals are such as to make

TABLE V—CHEMICAL ABSTRACT JOURNALS OF THE WORLD

GERMANY	
Chemisches Zentralblatt.	
Chemiker-Zeitung.	
Zeitschrift fuer angewandte Chemie.	
Zentralblatt fuer Biochemie und Biophysik.	
Biedermanns Zentralblatt fuer Agrikultur-chemie.	
Neues Jahrbuch fuer Mineralogie.	
Zeitschrift fuer Untersuchung der Nahrungs- und Genussmittel.	
FRANCE	
Bulletin de la société chimique de France.	
Le Mois scientifique et industriel.	
Revue de metallurgie.	
ENGLAND	
Journal of the Chemical Society.	
Journal of the Society of Chemical Industry.	
UNITED STATES	
Chemical Abstracts	

coöperation between *Chemisches Zentralblatt* and foreign abstract journals only an initial step. Effective combination would necessarily include most of these other German journals. In France the *Bulletin de la société chimique* has fairly important industrial competitors in the *Le mois scientifique et industriel* and *Revue de metallurgie*. In England the field is about evenly divided. In the United States the *Experiment Station Record*

and *Science Abstracts* are so limited in scope as not to encroach upon the province of *Chemical Abstracts*.

The two propositions relative to abstracting recently suggested by an International Commission are (1) the publication of an International Journal of Abstracts in three languages; (2) the publication of three editions of an International Journal of Abstracts, *viz.*, in English, French and German.

No. 1 doubtless means that the abstracts should appear in the language of the original article when that language is English, French or German. Probably all other languages would be translated into German because the majority of chemical articles are printed in German. (According to statistics in *Scienza Gazeta* 50 per cent of all chemical articles are in German, 13 per cent in French, 27 per cent in English, and the remainder or 10 per cent in Italian, Russian, etc.) This is the method of the *Botanisches Centralblatt*, which is a rather small journal and has comparatively few readers in this country. It has been estimated by one of the professors of botany at Ohio State University that not more than 300 men in this country make consistent use of this journal and that those who do are research men who can probably read French and German readily. When we consider that there are now about 6700 American subscribers to *Chemical Abstracts* and that perhaps the same number of English chemists are taking an abstract journal (in 1912 the membership of the Chemical Society of London was 3,248 and of the Society of Chemical Industry 4,198) there is some objection to their being required to read 60 per cent of their abstracts in German and 13 per cent in French. The cost of *Chemical Abstracts* to each member of the American Chemical Society was, in 1912, \$5.24. Assuming that there was an international abstract journal (taking the place of *Chemical Abstracts*) published in accordance with plan No. 1, it would need to contain about 25,000 abstracts, of which 15,000 would be in German and 3,250 in French. Almost any of us would rather pay our \$5.24 and have our abstracts in English. The time lost in translating on the part of Americans and Englishmen might involve such an economic loss as to eliminate any possibility of saving due to coöperation in an abstract journal of this kind. But our international journal would approach so nearly in cost per member our \$5.24 that we would be required to do all this reading of foreign languages for almost nothing. The *Scienza Gazeta* figures that an international journal would cost one-third less per subscriber than *Chemical Abstracts* is now costing the members of the American Chemical Society, which would be equivalent to receiving \$1.78 per year for this extra work. We cannot but conclude that Dr. W. A. Noyes satisfied a great need and performed a valuable service to American chemistry when he established an American abstract journal.

But whether a saving of \$1.78 per member is possible is still a question. It is more in the nature of a good guess, we believe, than of a calculation. In going over our printing bills for 1913 and refiguring them on the basis of an abstract journal of the same size as *Chemical Abstracts* to be sent in lieu of the *Journal of the Chemical Society*, *Journal of the Society of Chemical Industry*, *Chemical Abstracts*, *Bulletin de la société chimique de France*, and *Chemisches Zentralblatt* we obtain as the total cost of printing and wrapping \$45,247. The number of copies needed would be 18,600 (see Table VI).

Since Table VI shows that the printing cost of an abstract journal is about 60 per cent of the total cost, this would give as the total cost of an international journal about \$75,000 and we have not considered the fact that the sending of the copies from Germany (it would probably be printed in Germany) to other countries would cost in postage about \$2,800 per year more than at present. This would make the total \$77,800 per year. The abstract journal would then cost each member \$4.18 per year instead of \$5.24, and still two-thirds

of it would be in a foreign language. If the printing cost is 66 per cent of the total cost, the cost per member would be \$3.83.

TABLE VI

	Total cost	Printing and distribution cost	Per cent of total cost.
Chemical Abstracts.....	\$32,596	\$19,562	60
J. Chem. Soc. ....	16,338	10,613	65
J. Soc. Chem. Ind. ....	\$23,593	15,606	66
Chem. Zentr. ....	21,027	11,784	52

Average, 61

But there remain several factors which have not been taken into consideration: (1) A movement of this sort would surely reduce the memberships of the various societies and thus raise the cost above the figures given. There are hundreds of members in the American Chemical Society alone who would not subscribe for a "mixed language" journal. (2) The discontinuance of *Chemical Abstracts* would necessarily mean an increase in cost of the *Journal of the American Chemical Society* and *Journal of Industrial and Engineering Chemistry* and other journals of which the abstracts are a part. (3) A part of the benefit of having an American abstract journal is that it helps financially almost 300 abstractors, makes them more familiar with the literature than they would otherwise be and keeps up interest in the Society. (4) American chemists (especially industrial chemists) seem to require abstracts from an American point of view and because of the different character of the chemical industries in the various countries doubtless the same requirement arises on the part of foreign chemists. This, Charles Baskerville has aptly stated: "I realize that it may be more desirable for us to write our own abstracts absolutely independently, inasmuch as we have our national way of looking at things." For this reason alone independent national abstract journals might spring up and compete successfully with an international periodical. (5) The above estimate of \$77,800 is made on the basis of 0.17 page as the average length of an abstract. The average length of an abstract for *Chemisches Zentralblatt* is 0.39 page, for the *Journal of the Chemical Society* 0.41, and the *Bulletin de la société chimique de France* 0.43. Using 0.35 page as the proper length of an abstract (for the other societies would doubtless not be satisfied with less; they would probably object to the conciseness of style and the abbreviations necessary in *C. A.* and would desire more detail), this would mean an increase in size of the abstract journal of 100 per cent over that which would cost \$77,800. If it is argued that the *Journal of the Chemical Society* and *Bulletin de la société chimique de France* have less material on a page than *Chemical Abstracts*, it should be remembered that *Chemical Abstracts* is printed in a style and size of type which makes the cost lower and that the \$77,800 estimate is based on the *Chemical Abstracts* type. An increase of 100 per cent in space would raise the printing bill to \$76,343 instead of \$45,247. To this must be added another \$2,800 postage to foreign countries, making \$79,143. But this is only printing and distribution expense. The addition of \$29,753 which we previously figured as abstracting, salaries and other expense (and which would be considerably too small for the proposed international journal) would bring the total cost of an International Abstract Journal similar to *Chemical Abstracts* to \$108,896. If it were only \$100,000, the cost per member, provided there was no falling off in members, would be \$5.37. The cost to American chemists was in 1912 \$5.24.

It is evident from the foregoing that, disregarding the question of the desirability of an international abstract journal and confining ourselves to the economic phase only, the proposition in accordance with plan No. 1 is not attractive. May we suggest to its advocates that they should begin their discussions concerning it with a consideration of the scope of the proposed journal and the average length of its abstracts?

Plan No. 2 contemplates the publication of English, German and French editions of an international abstract journal. In discussing plan No. 1 we gave all possible advantage to the co-operation idea by assuming that the subscription list would be the combined subscription lists of the present journals, or 18,600. It will be best to note, however, that there are perhaps 1200 subscribers to the *Journal of the Society of Chemical Industry* in this country who also take *Chemical Abstracts*, and the duplication of purchasers of the *Journal of the Chemical Society* and *Journal of the Society of Chemical Industry* will probably amount to 2,000. Therefore we believe it fair to say that the subscribers to the international journal would number in the United States 5,000 and in England 5,000 (instead of more than 7,000). Such a comprehensive abstract journal in the German language ought to raise the German subscription to 3,000 and the French to 1,100, making a total of 14,100 subscribers or members of the international association. But again the question of scope of the journal and length of abstract is of paramount importance. If the average journal is to be as complete as *Chemical Abstracts*, it will cost: for printing the English edition about \$42,202; for the German edition about \$21,379; and for the French \$15,687; on the basis of 0.35 page per abstract. Using the same low figures as before for editing, etc., and adding to abstracting cost \$4,000 for translating abstracts into three languages, the cost of the entire journal per member per year for the members of the international association would be \$8.26. If American chemists are to profit financially from any such co-operation it will have to be through retrogression in regard to completeness of the abstract journal, which is surely not desirable. In order to hold the cost to the figures given, however, the other societies would have to permit the extensive use of formulas and abbreviations such as are now used in *Chemical Abstracts*. This is a question which must be settled before accurate costs under either of these plans can be ascertained.

But there are other objections to plans Nos. 1 and 2, in that both require the collecting of the copy at one office and redistribution of the printed material from that point. Aside from the excess postage cost there is the disadvantage of delay involved. For example, now we can abstract American journals within a few days of publication and have the abstracts to our members in a few weeks. The Germans can do likewise with their periodicals, and so can the French. Under the proposed scheme Americans or Englishmen could not receive abstracts from their respective journals until the trip to Europe and back had been made and under plan No. 2 these American and English abstracts would necessarily remain in the central office until translated. All abstracts would under plan No. 2 have to be held up until translations were made and then printed simultaneously with the translations.

There seems to be a point at which centralization becomes a nuisance and we believe this point is reached when we try to cross the language line or span the ocean.

The Esperanto idea will not be discussed in detail for two reasons: (1) We are told that Esperanto is not flexible enough to meet the demands of chemistry. (2) If there is to be a unification of languages for chemists throughout the world, the place to start the same would best be in the college or university, then print all chemical journals in the one language and finally use this language in the abstract journals. Unless all the chemical periodicals are printed in the one language, it means simply the learning of a new language for the sake of reading the abstract journal. And for what end? There might be a saving of \$1 or \$2 per year per chemist by issuing only one journal, but economy is not the goal of life.

In our opinion the solution of this problem lies in letting each society do as it sees fit about the abstracting question. It would not be right to force a member of the London Chemical



Society to subscribe more to an international journal than he is now paying for the *Journal of the Chemical Society* abstracts just because the American chemists will not be satisfied with an incomplete abstract journal or because the Germans want longer abstracts. Each of the leading abstract journals is superior in some respects to the others and is subscribed to by those to whom this superiority appeals. Each phase of the abstracting is emphasized in some one of these journals so a chemist has his choice and gets what he wants at a less cost than if all abstracts were reduced to a dead level and he had to buy everything that anyone else might desire.

The proposition that appeals to us more than anything is suggested by an announcement in the *Proceedings of the London Chemical Society* to the effect that representatives of the *Journal of the Chemical Society* and the *Journal of the Society of Chemical Industry* were to meet to discuss coöperation in England alone. This is feasible because of the unity of language and land. And for the same reason, if *Chemisches Zentralblatt*, *Chemiker Zeitung*, *Zeitschrift für angewandte Chemie* and other German abstract journals should combine there would be greater economy and greater satisfaction than in any possible kind of international journal. In France the *Bulletin de la société chimique de France* might combine with *Le mois scientifique et industriel*.

In closing we would suggest that there is a possibility of saving a little abstracting expense for each abstract journal and that broader coöperation to that extent may be practicable. It could best be attained by having the abstract journals exchange, without charge, their corrected page proofs. Then if there is any advantage in copying or translating abstracts instead of taking the abstracts from the originals, the practice could be followed to that extent. There would be nothing compulsory about it, and any practice which proved unprofitable could be discontinued summarily and without confusion. It would mean coöperation whenever coöperation is beneficial; at no other time is it desirable.

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## THE PRESENT STATE OF THE CYANAMID INDUSTRY<sup>1</sup>

By E. J. PRANKE

Cyanamid is a dry, grayish black pulverized material, which is made by combining pure atmospheric nitrogen with calcium carbide at a temperature of 1100 to 1200° C. Its principal use in this country is as a source of nitrogen in mixed fertilizers.

Fertilizers have an intimate relation to the cost of living that should be more generally recognized. It is a well known fact that the cost of living has increased in this country at a much more rapid rate than it has abroad. When we consider the facts closely, we find that the extraordinary increase in this country has been in the cost of food products, while other than foods have increased at only the general rate prevailing throughout the world. From 1900 to 1910, for instance, all commodities in this country increased in cost about 26 per cent, as compared with 9 per cent in England, and 12 per cent in France, or 15 per cent in the world, including the United States. But other than foods in this country increased only 17 per cent, while foods increased 35 per cent, or more than twice as much. While population increased 21 per cent in the ten years, crop production increased only 10 per cent.

The rapid increase in the cost of foods in this country must be checked by increased crop production, just as food prices are held down in the more densely populated European countries; the yields per acre must be increased. In Europe the yields of the staple crops average from 50 to 100 per cent larger per acre than in this country. Crop rotation, seed selection, and thor-

ough cultivation are estimated to be responsible for one-half the increased yields, while the use of fertilizers is considered, by competent authorities, to cause as much increase as all other factors put together. The countries of highest agricultural development are the largest consumers of fertilizers. Germany, for instance, spends as much money per annum for fertilizers as we do, although she has only  $\frac{1}{13}$  of the acreage under cultivation that we have. This, moreover, is in a country of abundant cheap farm labor, which would indicate that mere muscle cannot take the place of plant food in the growing of crops.

The development of an increased use of fertilizers in this country is mostly a matter of education of the farmer, and to some extent a matter of fertilizer prices. The farmer must be taught that there is a right way and a wrong way to buy and use fertilizers, and that the right way is profitable; the wrong way may or may not be. A lower price, however, will always make it easier to earn a profit, and the lower the price the larger the profit, the greater the incentive to use fertilizers, and the larger the crops produced. Hence, any improvement in the art of manufacturing fertilizers or fertilizer materials that will make them cheaper, will ultimately lower the cost of foods, and hence, the cost of living.

Any considerable reduction in the cost of fertilizers is hardly to be expected, however, unless it takes place through a reduction in the cost of the most expensive ingredient, nitrogen. The price of phosphoric acid is now probably about as low as it will ever be. The main source of this ingredient, namely, phosphate rock, is found in enormous deposits that will last a great many years. The present method of treatment would seem to be about as economical as any that is likely to be devised. So with potash. Practically all of our potash is imported from Germany, where it occurs in great natural beds that will last for many thousands of years at the present rate of development. It is true that lately there has been considerable talk of obtaining potash by the incineration of a sea-weed, known as kelp, found in abundance on the Pacific coast. Whether potash from this source can be produced and shipped to the Eastern part of the United States at a much lower cost than the German potash can be delivered remains to be seen. A pound of nitrogen costs about four times as much as a pound of phosphoric acid or a pound of potash. The cost of the nitrogen in the average fertilizer makes up about 45 per cent of the total cost. The higher price paid for nitrogen, however, is justified by the fact that this is the element usually most needed to increase the productivity of the average soil, and moreover, its application seems to be in most cases a prerequisite for the effective utilization of the other ingredients, phosphoric acid and potash. A typical instance is found in the results of 55 years of continuous experiments on wheat in England, at the Rothamsted Experiment Station. These are as follows:

FERTILIZER	PER ACRE	
	YIELD	INCREASE
None	12.9 bu.	
Phosphate and potash only	14.8 bu.	1.9 bu.
Nitrogen only	20.5 bu.	7.6 bu.
Nitrogen, phosphate and potash	31.6 bu.	18.7 bu.

Fertilizer nitrogen may be classified according to its sources, into organic, derived from animal or vegetable matter, and inorganic, derived from mineral sources. The price of the organic ammoniates, chief of which are cottonseed meal, tankage, dried blood and dried fish, is steadily tending upward. This is due principally to the decreased per capita production of animal and vegetable products in recent years, and to the increased uses to which by-products are applied. Recently, the above by-products were used mostly in fertilizers, now they are used to a considerable extent in stock foods. The inorganic ammoniates, chief of which are sodium nitrate, ammonium sulfate and cyanamid, have lately been suffering a general decline in

<sup>1</sup> Presented before the Nashville, Tenn., Section of the A. C. S., February 20, 1914.

prices. The general price level of this class of nitrogen is about the same as it was ten years ago, in spite of the increase of about 26 per cent in the cost of all commodities in that time. The lower prices now prevailing are undoubtedly due to the rapidly increasing production of inorganic ammoniates. Probably the most important single factor in this movement is the production of cyanamid.

In this country the demand for cyanamid has kept pace with the supply at the current prices for inorganic ammoniates, and sometimes at higher prices. Yet, this fact has led some of those who stand in the position of advisors to the farmer to assert that they cannot recommend a new material until its advantages have been proved superior, and in addition its prices made lower than that of the older ammoniates. They overlook the fact that no industry in the early stages of its development has turned out as perfect a product at as low prices as was later found possible. Pioneering is always costly, and a pioneer industry must have the support of the public from the start in order to develop at all. It is the history of great manufacturing enterprises that where the support of the public has been accorded, the final benefits to the public are out of all proportion to what could have been expected in the beginning. The only question that broadminded men should ask, is: Has the process inherent merit? Will it prove to be a great public good? With regard to the cyanamid process the answer must be: Yes. The cyanamid process is probably the cheapest known process for producing a commercial nitrogen compound on a large scale. It is only a question of time until an ideal product is developed, and sold at the lowest prices. In the meantime, however, the industry must have the support of the public. Fortunately, it has this support now, as is evident from a glance at the statistics.

In 1904 the world's production of cyanamid was 5,000 tons. In 1909 it was 50,000 tons. In 1914 it will be 275,000 tons. The American Cyanamid Company began operations at Niagara Falls in January, 1910, with a capacity of 12,000 tons per annum. This was increased in 1913 to 32,000 tons per annum. Further extensions, which will reach completion in April, 1914, will make the yearly capacity of the American plant 64,000 tons. The world's output of cyanamid brings at wholesale prices about \$14,000,000 per annum, the European product being of somewhat higher nitrogen content than the American.

Now if one were to turn to the literature on cyanamid, and on the basis of what he reads there, hazard an opinion as to the rate of growth of the industry in the past ten years, he would probably fall far short of the truth in his estimate. If the literature were taken by the public as the sole basis of judgment of the value of cyanamid as a fertilizer, it is doubtful whether there would be enough cyanamid sold to keep one small factory busy furnishing the world's supply, instead of the fourteen large factories with their output of fourteen million dollars worth of product per annum. It is conceivable that a small amount of an inferior material might be disposed of by clever salesmen for one or two seasons, but the fact of such steady rapid growth as the cyanamid industry has made is inconsistent with essential inferiority. The fact is, that the great majority of limitations that have been attributed to cyanamid simply have no bearing upon the practical use of the material. Some of the limitations mentioned in the literature do not exist at all, while the practical significance of others is found, on examination, to approach zero in value.

Advancement in the knowledge of a substance begins when its properties are expressed quantitatively. Practically all of the problems of the early days of the cyanamid industry have been solved by paying attention to the quantities involved. Let us now consider some of the characteristics of cyanamid that have been claimed in the literature to be disadvantageous, and let us note in each instance how the supposed difficulty was solved.

#### CALCIUM CARBIDE

This substance was occasionally found to the extent of several per cent in the material produced in the earlier days of the industry abroad. It is now entirely removed in the course of manufacture by the addition of sufficient water to entirely decompose it. The American practice of hydration makes the presence of undecomposed carbide impossible. In Europe, the last step before shipping the material is to test for carbide.

#### CHANGE IN WEIGHT AND SUPPOSED LOSS OF NITROGEN IN STORAGE

On exposure to the air, cyanamid absorbs moisture and carbon dioxide, which makes it weigh more. As the total weight increases, the percentage of nitrogen will of course decrease. The new weight, however, multiplied by the new percentage of nitrogen will show the same number of pounds of nitrogen present after storage as there was at the beginning. Early observers noted the decrease in nitrogen analysis, but failed to take account of the increase in weight; hence they reported large losses of nitrogen. All attempts, however, to show a loss of nitrogen in goods stored in factories have failed, when the final weight of the pile was determined, as well as the analysis of a sample drawn in a uniform manner from all parts of the pile. When storage is desirable and necessary, it is a relatively simple operation to draw a practical average sample for analysis at the conclusion of the period of storage. It should be mentioned here too that other fertilizer materials are by no means perfect in respect to their storing qualities. The practical man, however, does not ask for perfection; it is usually too difficult of attainment, and too costly and often quite useless. All that is required is that a thing be good enough for the purpose.

It is true that laboratory experiments have shown that when a few grams of cyanamid are exposed in a thin layer to a constantly saturated atmosphere of moisture for a long time an odor of ammonia is given off, and a loss amounting to about 0.02 per cent of the total nitrogen for each 1 per cent gain in weight of the exposed sample can be detected after allowing for the increase in weight. It is doubtful, however, whether this has any practical significance. The fact that iron filings will rust over night in a damp atmosphere does not prevent the use of iron for building bridges or other structures exposed to damp weather. The fact that iron filings are readily burned by dropping them through the flame of a match has not prevented the use of iron as a non-combustible building material. Even assuming that the severe conditions of the laboratory experiment with cyanamid could be applied to conditions of factory storage, the loss of nitrogen would be insignificant. In factory storage cyanamid gains in weight on an average only about 1 per cent a month. Hence a material containing 16 units of nitrogen would contain, after one month, somewhere between 15.997 and 16.000 units. To the practical fertilizer man such differences are inappreciable. Even in one year, at this rate, the loss would be only 0.036 unit of nitrogen. The best fertilizer analyses for nitrogen, however, have no meaning within 0.100 per cent, and sometimes 0.200 per cent. As a matter of fact the immaterial loss of actual nitrogen from cyanamid is probably much less than the actual losses known to occur in the decomposition of organic fertilizer materials in storage. All these are so insignificant that nobody pays any attention to them.

#### DUST

Attention has often been called to the dustiness of the powdered cyanamid, and to its caustic action on the skin and mucous membranes. In some fertilizer factories loosely constructed elevators and mixing machines, and open screens permit the escape of the fine material, which settles on the exposed parts of the laborer's body. If then the laborer fails to wash the dust off at the conclusion of the day's work, the lime compounds will absorb moisture and probably some of the natural oils from the skin, and cause some irritation. If, however, the laborer will

rub any kind of oil or grease on the exposed parts of his body before he commences work, and will use oil or grease again at the conclusion of the day's work, he will find that the dust will not burn during the day, and is very easily wiped off when he is through with his work. Of course the dust must be removed from the skin at least once a day. Laborers who work in the factories where cyanamid is made never have skin irritation. They take the simple precautions that have just been described.

It is a peculiar fact that when alcohol is taken the into body after one has breathed cyanamid dust, there follows within a few minutes a reaction colloquially known as a "flush." This is characterized by an increased flow of blood to the skin of the upper part of the body, deepening its color, and giving a suggestion of swelling. The subject also has a feeling of oppression in his breathing. In no case has anyone ever been known to suffer harm from a "flush," but only temporary discomfort, the degree depending upon the amount of alcohol imbibed. The effects usually pass away within an hour after taking the alcohol. Moreover, alcohol is the only known cause of this effect of breathing the dust. Total abstainers never experience the "flush."

In the better equipped fertilizer factories, the machinery is enclosed in such a way that practically no dust escapes. As soon as the cyanamid becomes a part of the mixture the dust is effectively laid by the large excess of other materials, many of which are naturally damp.

#### GRANULATED CYANAMID

During the past year there was placed on the market in this country a granulated cyanamid, which is practically free from dust. This material is made by pressing damp cyanamid into briquets, which after hardening are ground, and the product screened to sizes between 15- and 60-mesh sieves. On the basis of the original estimated cost of granulating, this improved product was sold at a premium of seven to eight per cent over the price of the powdered material. Actual operation records show, however, that the cost of granulating is more than double this amount. When the price of granulated cyanamid was advanced sufficient to cover the manufacturing expense of producing it, the demand practically ceased. Consumers apparently will not pay a premium of fifteen per cent for dustless material.

#### AGRICULTURAL USE AND VALUE

Perhaps the most important question that can be asked about cyanamid is: What is its fertilizing value? Does it give to the farmer year after year a consistent profit on his investment, that compares favorably with the profit on an equal expenditure for some other material?

One way to answer the question is to fertilize one-third of a field in the ordinary way with a properly compounded commercial cyanamid mixture, fertilize another one-third with some other standard mixture of equivalent analysis, and omit fertilizers from the remaining one-third. The answer given by such an experiment usually is that cyanamid may be profitably substituted for an equivalent amount of nitrogen in other standard forms.

Unfortunately, a commercial fertilizer mixture is usually regarded by the orthodox scientific investigator as too complex to fit into the logical scheme of his fertilizer test plats. He wants to test the unmixed cyanamid, and he usually wants to use it in quantities far more generous than any that the farmer would ever think of applying. The results of his small plat or pot experiments often do not agree with the farmer's field experience. There are four principal reasons for the difference: (1) Excessive applications of any of the common inorganic ammoniates may cause injury to the plants, and cyanamid is somewhat more active in this respect than the others, (2) cyanamid behaves agricultur-

ally like an organic ammoniate and is not strictly comparable with the other inorganic ammoniates, (3) certain mixtures of two or more different kinds of nitrogen usually give a larger yield than the same quantity of nitrogen in one form alone, and (4) the cyanamid in commercial mixtures is transformed by interaction with phosphates, and loses its identity.

The farmer's use of fertilizers in general is guided solely by the profits derived therefrom. He is continually seeking to learn in what way and in what amounts he shall apply his fertilizers so as to derive a maximum profit. The broad result of this general searching for the best ways is the formation of certain standards of fertilizer practice. These standards are in actual operation on the farms where the most money is being made. For the great staple crops, wheat, oats, corn, hay, and cotton, the application of nitrogen gives increasing profits up to the point where about 200 lbs. of cyanamid or the equivalent thereof in other forms is applied per acre. Above this amount of nitrogen, additional applications will produce additional yields but the value of the extra yield will not, except in the case of very good soils, exceed the extra cost that it took to produce it. Now if cyanamid produces satisfactory results with this maximum economical application, what reasonable objection can there be if it does not produce satisfactory results when used in quantities from two to four times as large? Yet objections have been made against it, based upon such excessive applications in small plat or pot experiments.

The effect of excessive applications of unmixed cyanamid is more evident on acid light sandy soils than on any others. This is probably due to two causes: first, the absorbing power of such soils is low, since the coarse soil particles do not present the large amount of surface that is offered by the much finer particles in the loam and clay soils; and second, bacteria are notably deficient in such soils. The remedies for this situation, if it is necessary to use the unmixed cyanamid, are two: *first*, not more than 250 lbs. of cyanamid per acre should be applied, either spread broadcast and worked well into the soil, or if applied in rows, put down in two applications; *second*, the acid soil conditions should be removed and the bacterial condition improved by the use of sufficient lime, before fertilizing or as a part of the fertilizer. In other words, the object is to avoid too high a concentration of cyanamid in any one portion of soil, and to favor the conversion of the cyanamid to other forms of nitrogen.

Practically, there is no more necessity for applying excessive quantities of one kind of ammoniate, than there is for feeding an animal an excessive amount of one kind of food. There are stock-foods, green clover, for instance, that may kill an animal if fed to excess at one time, and there are many articles of human food that will cause serious illness if eaten to excess, but that is no objection to their use in normal economical quantities. When it is necessary to apply large quantities of nitrogen to certain crops, such as truck crops, potatoes, fancy tobacco, etc., it is customary and desirable to derive the nitrogen from several sources, and not from one only. The use of 200 lbs. of cyanamid per acre in rows, or 300 lbs. broadcast would be economical and satisfactory on such crops, but additional nitrogen should be derived from other sources.

Experience has taught the practical fertilizer manufacturer that a mixture of different forms of nitrogen, properly chosen, almost invariably gives better results than an equivalent amount of nitrogen in a single form. It is well known that different ammoniates yield their nitrogen to the plant in an available form at much different rates, depending upon the nature of the fertilizer, soil conditions, climate, etc. Thus, with respect to the rapidity with which they yield available nitrogen the common ammoniates may be arranged in about the following order, beginning with the most rapid:



- |                        |                            |
|------------------------|----------------------------|
| 1—Sodium Nitrate.      | 4—Dried Blood, Dried Fish, |
| 2—Ammonium Sulfate.    | Tankage.                   |
| 3—Cyanamid, Cottonseed | 5—Steamed Bone, Ground Raw |
| Meal, Castor Pomace.   | Bone.                      |

When applied at the usual rate the quick-acting ammoniates supply an abundance of nitrogen in the early stages of growth, but little or none in the last stages. The slow-acting ammoniates do not supply an adequate amount of nitrogen in the early stages, while those of medium activity are ineffective both in the beginning and in the final stages of growth. It is obvious that a mixture of ammoniates that will furnish a uniform stream of available nitrogen from the beginning of growth to maturity will produce better results than a single ammoniate of equal nitrogen content that furnishes an over-supply of available nitrogen at one time and is deficient at other times.

The above applies only to the economical fertilizing of plants, where just enough nitrogen is added to supply the plants' requirements. Where there is a great excess of nitrogen applied, there is almost certain to be a sufficient supply to meet the plants' requirements at all stages of growth. Even the most active form of nitrogen would last longer than the period of growth of the plant if enough were applied at the start, but such applications would not be economical on account of unavoidable losses.

The common practice, therefore, of estimating the relative value of different ammoniates by measuring their results when applied to a common task is not strictly accurate. Fertilizer materials have as much individuality and are as different in their functions as are different kinds of building material, or different breeds of horses, or different kinds of clothing. Some excel in one respect, and others in another respect. Cyanamid, for instance, may take the place of the organic ammoniates of intermediate activity, because the nitrogen in these materials becomes available at about the same rate, and under the same conditions as cyanamid nitrogen. It cannot, however, act as successfully as sodium nitrate, when the object is to produce forced growth, because cyanamid is not in the class of forcing ammoniates. The fact that a draft horse cannot travel a mile in three minutes argues very little as to his ability as a draft horse.

The great majority of the reports on the fertilizing value of cyanamid as found in the literature, therefore, have little significance for the American manufacturer of fertilizers. The question to which he wants an answer has been very little touched upon. This is: "What is the effect of putting cyanamid in place of one or more of the other ammoniates, especially the expensive organic ammoniates, in fertilizer mixtures?" From observation of practical mixtures, however, the answer is, that cyanamid is a successful substitute for the medium to slow-acting organic ammoniates.

Another reason why results with the pure cyanamid may not hold for the actual cyanamid mixtures sold in America is found in the fact that practically all the cyanamid used in this country is sold to fertilizer manufacturers, and practically all of it is used in acid phosphate mixtures. A very little is used in basic slag mixtures, and a small amount in other ways.

When cyanamid is mixed with acid phosphate there is an immediate reaction, resulting in the complete breaking down of the calcium cyanamid. The calcium is fixed as mono- and di-calcium phosphates—the nitrogen is hydrolyzed to urea. Urea, from the fertilizer standpoint, seems to be the ideal form of organic nitrogen. It is extremely soluble, can be directly assimilated by plants, but if not immediately absorbed, reacts with the soil particles, and becomes fixed as rather insoluble double ammonium salts, that do not easily wash out of the soil. By this chemical reaction therefore, the identity of the original cyanamid is destroyed, and a new set of properties is established, namely, the properties of a mixture of urea nitrogen with mono-

and di-calcium phosphates. This is what the American farmer gets when he buys a commercial cyanamid mixture made with acid phosphate as the source of phosphoric acid. The practical results from such mixtures are, as one would expect, entirely satisfactory.

Basic slag mixtures are used to some extent in the states along the Atlantic Coast. On acid sandy soils basic slag is probably somewhat more effective than acid phosphate, probably owing, in a large measure, to the action of the lime in neutralizing soil acids, and permitting the restoration of bacteria in proper numbers. Slag contains from 15 to 18 per cent iron, and about 5 per cent manganese, both of which are powerful catalyzers of cyanamid to the urea form. The practical experience with these mixtures seems to be entirely satisfactory.

We see, therefore, that practically there is no need of applying more than 200 lbs. of unmixed cyanamid per acre at one time on the staple crops, or 300 lbs. per acre on truck crops. If more nitrogen than this is needed, it should be derived from additional sources. The great majority of the reports found in the literature on cyanamid are practically worthless because the experiments were made with excessive quantities. The only thoroughly satisfactory and valuable test from the farmer's point of view, is one that conforms to the economic requirements that govern the use of any fertilizer, and is made under practical farm conditions. Since practically all the cyanamid sold in this country reaches the farmer as a mixture of urea nitrogen and mono- and di-calcium phosphates, it is only necessary to know what results are being obtained with such mixtures. The reports are almost unanimously favorable.

#### MIXING WITH ACID PHOSPHATE

The statement can be found in many places in the literature that "Cyanamid must not be mixed with acid phosphate, since thereby the available phosphoric acid is converted to the insoluble form." On charts showing incompatible mixtures of fertilizer materials, the mixtures of cyanamid and acid phosphate are always indicated as not practical. Nevertheless, as was said above, practically all of the cyanamid sold in this country is used in mixtures containing acid phosphate.

In the average phosphate most of the phosphoric acid is in the water-soluble condition (as free phosphoric acid and mono-calcium phosphate), a small amount is present as di-calcium phosphate, not soluble in water but soluble in ammonium citrate solution, and a small amount is present as phosphates insoluble in ammonium citrate solution. When a small amount of cyanamid or other active lime compound is added to acid phosphate, there is an immediate reaction between the lime and the water-soluble phosphoric acid, resulting in a change of the latter to the citrate-soluble form. Both of these forms have about the same agricultural value, and both have the same commercial value. When a large amount of cyanamid is added to acid phosphate, however, there is a more complete neutralization, resulting in the formation of forms containing more lime than di-calcium phosphate contains, and these forms are not soluble in citrate solution; hence, they have no commercial value.

Now it happens that the experiments reported in the literature were mostly made with large quantities of cyanamid, hence the results were unfavorable to such mixtures. On closer investigation of this problem, however, paying attention to the quantitative factors involved, it was found that as the quantity of cyanamid used with respect to the acid phosphate decreased, the loss of available phosphoric acid decreased. When the quantity of cyanamid is as small as 60 to 80 lbs. of cyanamid to a ton of average complete mixture containing approximately 1000 lbs. of acid phosphate, the loss of available phosphoric acid is not appreciable. It is at this rate that most of the cyanamid sold in this country is used in commercial fertilizers. In some cases as much as 150 lbs. is successfully used. The acid phosphate must be dry in this case, and as much bulky organic matter as possible used.

## MIXTURES WITH AMMONIUM SULFATE

It has also been said that cyanamid must not by any means be mixed with ammonium sulfate, since the lime in the former will drive out free ammonia from the ammonium sulfate. This is true if we consider a simple mixture of only the two substances. It is also true for mixtures of cyanamid, ammonium sulfate and acid phosphate, if large quantities of cyanamid are used. If, however, we pay attention to the quantitative factors again, we find that when there are not more than 150 lbs. of cyanamid present along with ammonium sulfate and 1000 lbs. of acid phosphate, there will be no escape of ammonia from the mixture. The ammonia set free by the lime is caught by the acid phosphate, and fixed as ammonium phosphates. Since the use of acid phosphate with cyanamid imposes a limit of less than 150 lbs. of cyanamid per ton of mixture it is not possible to reach a large enough quantity of cyanamid in such mixtures to cause a loss of ammonia. Hence, in all commercial acid phosphate mixtures, made with due regard to the necessity of keeping the phosphoric acid available, there is no possibility of liberation of free ammonia.

## SPECIAL ADVANTAGES

It may not be amiss here to name the special advantages that commend the use of cyanamid to the fertilizer manufacturer: (1) It is a low-priced material; (2) It has a powerful drying-out action on damp materials used in mixtures; (3) It removes free acids from the acid phosphate, thus preventing rotting of bags, and loss of nitric acid from sodium nitrate in the mixture; (4) It adds agriculturally available lime to the mixture; and, (5) It can successfully replace part or all of the more expensive organic materials in a fertilizer.

## SUMMARY

I—The cost of food products in the United States has increased about twice as fast as the cost of other commodities, and about twice as fast as the general cost of living throughout the world. This tendency can be offset by an increased crop production, which will lower the price of food products, and hence the cost of living. Fertilizers are the most important single factor in increasing the crop production.

II—Nitrogen is the most expensive and agriculturally most necessary element in commercial fertilizers. A general reduction in the cost of the latter must come through increased production of nitrogen at lower cost. The cyanamid process is probably the cheapest known source of fertilizer nitrogen.

III—The rapid successful development of the economically important cyanamid industry has been full of difficulties, practically all of which have been overcome or minimized by paying attention to the quantitative factors involved.

IV—The greatest common error in the experimental testing of cyanamid has been in the use of excessive quantities. When used in normal agricultural quantities, the results are entirely satisfactory.

V—All difficulties from the farmer's standpoint are removed by the complete reaction of the cyanamid with acid phosphate in commercial mixtures. Such mixtures consume practically all of the American output of cyanamid.

VI—Cyanamid has several special advantages as an ingredient in mixed fertilizers.

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## INDUSTRIAL MALTOSE

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It is common knowledge that literature records numerous instances of checks or lapses in the development of various industries or arts. In the field of starch products, the maltose industry is an example of this sort. Its existence has become so

obscure, as to have practically disappeared from the public eye.

An examination into this decadence, and as to whether or not it has been a simple case resulting from a survival of the fittest, seems very timely, especially because of its direct bearing on the justifiability of glucose, which, as a product and as a commercial term, is still in active controversy. Sufficient references will be found appended to supply an introduction to the existing literature.

With the possible exception of Japan, where malt-converted or maltose products have been highly esteemed since remote antiquity, cane sugar has generally served as the standard of artificial sweetening, from a very early time. About the beginning of the nineteenth century, owing to the high cost of the established industrial sugar and the persistence of the sweetening habit, attention became effectively awakened with regard to possible substitutes.

This condition became greatly intensified in Europe. About the year 1809, France felt the vital need of some new commercial product that would more or less replace or "piece out" cane sugar. This particular situation was a result from the bearing of the Empire's prolonged conflicts with England upon its supply of Colonial sugar. Ingenuity and invention were stimulated by means of national premiums offered for cane sugar substitutes, and the grape was very hopefully regarded as a source from which an easy and abundant supply of "saccharine matter" could be had. In fact, the first prizes were directed toward competition in respect to syrups and sugar from grapes. A little later, as this source was found to be impracticable, special inducements were extended to cover any one who might discover "the easiest and cheapest process for making syrups, which shall be most like those from cane." Thus it was a general but more particularly a National necessity which demanded a cheap and easily obtainable substitute for cane sugar. Without a doubt these were the stimulating incentives that led to the discovery of the availability of starch as an economical source of syrups and solids which were more or less sweet.

The acid process for the "saccharification" of starch, or rather of starch pastes, was the first in the field. Credit for this discovery and the consequent facilitation of an industry dealing with the commodity now so long known as glucose, is generally conceded to Kirschhoff, in the year 1811. The principle of action upon which this process depends is a non-selective or general one—that is, as opposed to specificity—and essentially for this reason it was relatively simple to develop its practice to a point where the products were easy and cheap to produce as compared with cane sugar.

When the Continental Blockade was raised, the pressure of necessity for sugar substitutions was very materially reduced. The impetus, however, already given to the glucose industry, sufficed to establish a stronghold for it upon the imagination and life of the people. The idea was especially attractive, because of the great novelty of a ready supply of cheap, sweet products of great apparent prospects. The development of the beet sugar industry likewise exerted a sharp influence in minimizing the popular demand for sucrose substitutes. At this period it should be remembered that the science of carbohydrates and proteins was in its infancy, as was also true of dietetics and physiological chemistry.

It was not until very considerably later that the European maltose industry began to spontaneously develop; that is to say, its inception quite lacked the special features of forced opportunity and the support of an ovation accompanying an apparently unique realization, under which the glucose process was conceived and fostered.

The characteristic sugar of malt-converted products, more difficult to study than the sugar glucose, was not discovered by De Saussure until the year 1819. It remained until 1847 but imperfectly discerned, when Dubrunfaut carried recognition



very much further and gave to this carbohydrate individual the name maltose which it now bears. Although this well defined work upon the part of Dubrunfaut became obscured and the facts were not rediscovered by O'Sullivan until later years, nevertheless, Dubrunfaut himself seems at the time to have had some very clear impressions in regard to the nature and significance of the syrups and sugars which starch was capable of yielding.

However, this may have been, industrially speaking, except with regard to Japan, it is to Dubrunfaut that credit appears to be due as having been the pioneer in the development of malt-converted syrups and sugars. Cuisenier became associated with him, and it was mainly owing to these two workers that the application of the commercially designated maltose products reached the stage attained about the year 1883.

The establishment of glucose had introduced a new factor into a situation theretofore dominated by the products of the cane. The new physical properties of the starch syrup, that had become commercially entrenched, had led to a number of attractive developments in candies, confections, etc., not practicable before. Hence it was that maltose found itself competing in two totally different directions: with glucose against sucrose on the one hand, and on the other by itself against its starch derived predecessor.

Great difficulties were encountered. Although recognition of various merits of the new commodities was readily secured, the processes in use stubbornly resisted every attempt to equalize the manufacturing expense with glucose costs.

#### ANALYSIS OF PIONEER MALTOSE PROCESSES

The methods that have been and to a limited extent still are employed in the manufacture of industrial maltose may be divided, in a general way, into two classes.

One depended upon the use of very crude starchy materials such as ground maize, corn grits, etc., while the other, by far the less successful, apparently began operations with a more or less impure starch-flour. In either event large proportions of malt were required to effect amylolysis. From fifteen to twenty-five per cent of barley-malt (dry basis) reckoned on the starchy base may be taken as representing that industrial factor.

The general nature of the established processes is well known, and need not be particularized here. Details vary, but all include four essential manufacturing stages, namely, Aqueous Cooking, Saccharification, Refining, and Concentration; and these remain to be dealt with by any specific starch saccharification process yielding edible syrups and solids, except perhaps some future electro-magnetic method which may act effectively upon ungelatinized starch granules, in the presence of neutral or conducting water.

The basic materials were all thick-boiling. By this is meant that constituent starch granules were not modified: they remained in their original state as regards well known paste-forming properties. This was a fundamental impediment. It was not surmounted and from its very nature, as will be shown, its disadvantages could not be overcome.

The chemical and physical properties connotated by the thick-boiling type of the materials operated on, imposed a number of grave peculiarities upon the established processes. Owing to this, aside from the bearing of any other condition, it was mechanically impracticable to reach cooking concentrations which were at all comparable with the densities of first "light liquors" of the glucose industry. Especially was this the case when using more or less impure thick-boiling or unmodified starch itself, freed from the protecting influence of enclosing cellular tissue, thus allowing viscosity effects to fully develop. Such a factor of a greatly depressed limit to initial concentration, is fatal to any process wherein low cost of evaporations, and plant and labor minimums, are elements in economic practice.

Low as the mechanical limit was, it could not be utilized be-

cause of the restrictive influence of various chemical and physical properties associated with the thick-boiling character of the crude unmodified bases. Working concentrations, in terms of starch represented in the pastes, as established by cooking operations, needed to be held to a minimum, in order to insure good carbohydrate yields, even though more than liberal use of malt in subsequent treatments was resorted to. Higher initial concentrations lead inevitably and progressively to restriction of diastatic reactivity, and the presence of amylaceous end products or residues of a very slimy and refractory nature. These remainders (the old so-called insoluble starch-cellulose, etc.), in addition to entailing very material direct economic loss, adversely affected filtrations to a hopeless extent.

At this point it should be recalled that in dealing with aqueous starch pastes, in conjunction with characteristic barley-malt amylase (homogenous or composite as it may be) the early stages of amylolysis, comprising extension of simplification, hydration, and solution, are the most difficult for the enzyme to effect. It should also be remembered that restrictive limits or tendencies are encountered depending upon the conditions of existence of the starchy colloids, and more or less hydrated granule residues, that may contribute to the composition of any given paste.

It may be here generally stated, that the controlling conditions involved contain two factors which are to an extent independent and of different significance: one being the qualitative and quantitative extent of hydration of the complex starchy basis of the pastes, and the other the freedom, relative or actual, of the water present, a condition only in part associated with the total water.

Extensive hydration and great freedom of sufficient water are, of course, favorable to enzymic amylolysis, and these desiderata are facilitated by low cooking densities, as is well known.

Thus it was owing mainly to the above outlined circumstances, among them some not obvious or apparent in work conducted at ordinary laboratory concentrations, that in the best practice the use of thick-boiling bases continued to require large proportions of malt and low cooking densities for even adequate completion of solution of the cooked pastes.

Use of large proportions of malt, as demanded by the irrational base, was an incurable disadvantage in itself. It was expensive in first cost. It contributed large percentages of objectionable nitrogenous and some other extractives to the sweet liquors in process, and this contamination alone sufficed to fix a quality of crudeness and carbohydrate inconsistency upon the finished products, despite elaborate and expensive refining. The business, moreover, was encumbered and handicapped in a number of ways, through the necessity of dealing with the excessive malt factor in a manner compatible with the conservation of a general enzymic agent and the recovery of an equivalent of its own associated starch.

Crudeness in the raw starchy materials, in lacking purity for the purpose, was an additional basic obstacle. The superfluous constituents tended to impede operations and promote losses in devious ways. In addition to the fact that they seriously increased the difficulty and cost of refining, in the end various contaminating effects could not be eliminated from the finished products. The large percentages and easily decomposable character of the major impurities present contraindicated any advantages that might have been apparent through acidic cooking, as a means of starch liquefaction in the manufacture of high-grade maltose products of great purity, for reasons that may be readily understood, though such considerations may very limitedly apply in alcohol and other manufacture.

It follows then that the practice of ordinary aqueous cooking, commonly under steam pressure, was a limit largely imposed by the impurity of the raw materials. It was, however, a defect of primary magnitude, owing to its leaving the starch paste and granule débris in such physical and chemical shape that



work of great difficulty still remained for the malt to do, requiring impracticably large percentages of that commodity.

An additional word may not be superfluous as regards the mechanical limits set to cooking as controlling initial concentration. Some exception might seem to exist in the case of comparatively pure starch or starch-flour in the unmodified condition. It might reasonably appear that acidic cooking should be advantageous in that instance, at least, as it might enable the starch equivalent content to be adequately increased by addition of the raw material during cooking, without exceeding mechanical practicability, because a free acidity would tend to maintain a thinning down effect upon the charge. The answer is that irrespective of the accentuation of evils already indicated that would follow from the application of a method of general hydrolysis to the crude impurities still associated with the starch, it is not advantageous to so influence the density of the cooking charge, inasmuch as to avoid incomplete cooking on the one hand, or overcooking on the other, hydrolytic action upon all of the cooking starch should begin and cease at substantially the same time. This requirement may be clearly recognized as imperative in connection with the enzymic manufacture of typical maltose products, as compared with the relatively unimportant influences of abnormal conversions carried out in glucose practice.

To sum up, it may be stated that the pioneer maltose processes, without exception, developed and declined while shackled by some or all of the limiting conditions which may now be outlined as follows:

1. The basic materials were all thick-boiling.
2. They were impure.
3. Cooking treatments were necessarily restricted essentially to disintegrating effects, and ordinary paste formation.
4. Prohibitive proportions of malt were required.
5. Soluble impurities, or rather undesirable organic and inorganic constituents, were introduced and developed during process to a ruinous extent.
6. Evaporations, size of plant for a given output, the labor involved, etc., were all excessive owing to unavoidably low initial concentration.
7. Refining was expensive and incomplete.
8. The products were crude and relatively costly, and hence of limited utility.

#### PARTIAL FAILURE OF GLUCOSE PROCESSES

As already mentioned the non-specificity of the principle employed in glucose manufacture made it comparatively easy to develop the resulting type of products so that they were cheap. This absence of specificity, however, results in the development of secondary and even more profoundly decomposing actions during the course of transformation of the starch and its associated impurities. Hence it is that notwithstanding the elaborate and disproportionately costly refining methods resorted to, as following easy first steps, advanced decomposition products remain in the finished glucose to a detrimental extent, along with the peculiar contamination contributed by the refining methods themselves. Moreover, the non-self-limiting action of acid hydrolysis as employed, engenders special losses in yield not shared in common with specific methods. These drawbacks, which are in excess of numerous other objections which are held by many to attach to the use of the glucosic type of starch products (whether acid hydrolyzed or not) as common foods, and certain technical defects to be mentioned later, have not been mastered after a century's continuous experience. The nature of the fundamental reasons and the inherent actions involved justify the statement, at this late day, that they are not likely ever to be mastered.

Efforts have been made to found methods and develop saccharine commodities free from the defects of acid saccharification processes and products, which should be independent of barley-

malt. The commercial exploitation of maize maltase, so as to enzymically manufacture glucose, is a case in point. None of these procedures have succeeded so well as those utilizing common diastase, nor have any held out the encouragements of that ancient agent in effectiveness, or in general dietetic desirability and type of results.

#### GENERAL PRINCIPLES BEARING ON RELATIVE ECONOMICS

Apparent simplification in procedure or detail is properly held to be a criterion of industrial advance. This principle, however, is not universal, because a real simplification in a process as a whole and a reduction in costs may be brought about by radical changes which, superficially considered, may seem not to bring the advance within the general rule. Moreover, as regards the manufacture of food products there are other criteria, and inherent standards, which in the last resort are quite extrinsic to adventitious business policies and artificial markets. It seems certain, however, that industrial maltose does not require that exceptions be invoked upon this score. Apart from other considerations, glucose manufacture, at least as it deals with maize, still retains an incubus in the way of secondary steps which are out of all proportion to the results secured, whereas, abolishment of the primary difficulties of pioneer maltose processes will automatically reduce refining to relatively simple and inexpensive means.

Although obvious, it may not be superfluous to point out that in earlier times, ordinary "green starch" (notably from maize) had not become an easy fact of industry, and that by-product economics had not taken on the remarkable importance of the present day. Certain limitations impressed upon the point of view of the older workers have disappeared. At the early time referred to, the idea of profitable carbohydrate yield seemed to be restrictively associated with the factors of extraction and saccharification in a direct attack upon the starch. Preliminary separations, or refinements, were considered to involve unjustifiable economic waste.

It seems important to remark the significance of the fact that this notion was also associated with glucose manufacture, remaining a formidable and unnecessary handicap until a very recent date, and to emphasize the circumstance that despite the late amelioration of this defect, so far as practicable, glucose manufacture remains heavily weighted by the requirement of excessive refining.

#### COMPARATIVE VALUE OF MALTOSES AND GLUCOSES

The author's activity in the subject being examined has covered a considerable period of time, and includes somewhat extensive experimental and small scale manufacturing work of an original nature, which will be discussed in a later paper. With the exception of the years 1896-7 and 1902, during which the preliminary experimental steps were taken in connection with the firm of Duryea & Co., in New York and in Sioux City, all the practical work referred to has been executed privately in the author's personal laboratories in New York, during 1904-5, and at Cardinal, Ont., during the years 1906-8, both inclusive. It seems ill-advised to omit to publicly record and submit what appear to be the more important results, conclusions, and views attained.

During the year 1896, the author became convinced that physiological or enzymically manufactured starch products of the maltose type were particularly adapted to direct dietetic uses, because of their natural constitutional suitability. The characteristic sugar and true physiological dextrins of such products seemed exceptionally well qualified to withstand bacteria as encountered in the stomach. In addition, they possessed a blandness and non-irritating quality with respect to the stomach lining by no means universally shared by common sugars. Moreover, while readily subject to normal enzymic completion of availability at the assimilative portions of the

alimentary tract, nevertheless they present conditions which require gradual actions; there can be no excessive rate and total of translation and delivery into the field of active metabolism at any point.

It would appear that these ideas, in agreement with much recorded at that time (1896), have been confirmed by the great preponderance of subsequent work in physiological chemistry and in dietetics. Enlightened science approves the normal.

About the year 1907, the author discovered that suitable maltose products possessed commanding technical advantages in the difficult and commercially important art of hard candy manufacture. In order of interest, at this juncture it may not be illogical to dwell briefly on this factor, as it may bear upon the future of industrial maltose.

Certain persisting difficulties associated with the manufacture and use of the glucose type of starch products—particularly acid-converted glucose—are tolerably well known. These are real defects, *i. e.*, are inherent in both manufacture and products. The extreme sensitiveness of *d*-glucose to merest traces of alkalies on the one hand, and the delicacy of sucrose in relation to acidity on the other, place glucose manufacturers in a quandary. The process employed makes it practically impossible to regularly produce products which are neutral from the points of view of both the *d*-glucose and sucrose, regarded as raw materials for hard candy-making, unless sophisticating substances are added. The familiar sulfurous friend of the glucose industry, colloquially known as "good old dope"—that is, sulfites in one form or another that are so used—thoroughly exemplifies the desperate character of the requirement in question.

While in principle maltoses resemble glucoses in relation to alkalies, as compared with sucrose, nevertheless in practice, according to the author's experience, the greater inherent technical suitability of maltoses for use in hard candy-making tends, in material measure, to protect these particular products from the mutability of typical physiological sugars. Moreover, as perhaps a matter of minor importance, maltose products, during manufacture, are not necessarily subject to heavy contamination by electrolytes—such as sodium chloride, thus in this case also being free from a well known misfortune of modern glucose. This particular defect of glucose results, of course, from neutralization of the hydrolyzing agent employed. In addition to the influence of NaCl on the palatability of saccharine products, it is generally recognized to have an inverting effect upon sucrose, under conditions of candy manufacture.

Aside from consideration of limitations in the manufacture of the ingredients used, hard candies must not only be dry and non-caramelized when made, but they must remain dry—that is, must not become sticky. Assuming everything else to be equal, typical maltose products of suitable type do not need sophistication, and tend to yield permanently dry candies, as contrasted with the divergent properties of glucose. That this is a basic condition is subject to proof by experimental candy manufacture using chemically pure *d*-glucose and maltose, as the author has done. Pure maltose-sucrose and pure *d*-glucose-sucrose candies stand customary cooking conditions equally well, and are very white and dry when made. Subjected to a test of artificial moistening, the author has found that such maltose candies dried out perfectly under usual room conditions and did not show any signs of "running." On the other hand the *d*-glucose candies, submitted to the same tests at the same time, exhibited a strong disposition to dissolve and spread, did not completely dry out, and remained sticky—until finally the free water was taken up by crystallization, quite ruining salable appearance. Glucose products tend towards deliquescence; maltose products exhibit a drying nature. It may be that in the presence of suitable other carbohydrates, and under appropriate conditions, the very strong bond for water which characterizes the sugar maltose

may lend itself to thorough non-aqueous saturation by means of carbohydrate compounding.

In brief, numerous practical candy-cooking experiments conducted in the author's laboratories and elsewhere have shown that good industrial maltose products stand cooking heats as well or better than the best glucoses; a given degree of hardness is reached at lower temperatures in the case of maltose; maltose candies present a more attractive appearance in the matter of surface glaze or luster; are blander and more luscious upon the palate—entirely lacking the somewhat acid after-taste of glucose; and finally, as contrasted with glucose, maltose candies remain dry under all ordinary atmospheric conditions.

It may be correctly said that the chemical individual maltose is not so sweet as *d*-glucose, which in turn is inferior to sucrose in this respect. Dealing with industrial maltoses and glucoses this seeming deficiency of maltose does not appear. Numerous comparisons on this score between products of approximately corresponding "conversions," for instance, maltoses of  $[\alpha]_D = 155^\circ$  and  $R = 0.70$  on the one hand, and glucoses showing about  $[\alpha]_D = 138^\circ$  and  $\kappa = 0.45$  for organic solids on the other, have demonstrated that the sweetness of the momentary first taste may be about the same, but substantially from that point on, in the act of tasting and consuming, the maltoses are indubitably sweeter. As thus compared without flavoring or admixture, high-grade industrial maltose syrups produce a profound impression of superiority upon the palate. The author believes the greater sweetness of the maltoses to be due to the true physiological type of the dextrin components and their ready reaction with salivary ptyalin, thus rapidly developing a large excess of total free sugar, as compared with the glucoses, upon the surfaces controlling the act of taste.

In addition to the factors determining the intrinsic value of the products, touched upon in the foregoing without exhaustion of the list, another and very general consideration remains which cannot be neglected. Whatever the reason or reasons may be, glucoses are universally recognized to be unattractive or unsuitable for use alone; improvement or disguise is a pre-requisite to sale and consumption, even in such a simple and direct application as involved in the case of table syrups. It is certainly a circumstance of extraordinary significance that commercial glucose, after a century of continuous effort and applied experience, should today occupy a surreptitious or submerged position among carbohydrate foodstuffs.

Finally, it is perhaps unnecessary to state that high-grade maltose syrups possess every physical advantage and keeping quality of the best industrial glucoses.

#### CONCLUSION

The examination embodied in this paper would seem to show that a modern revival of industrial maltose, if practicable, would present many advantages, and furthermore, that such a development is by no means fanciful, provided only that radical and correct solutions be found for pioneer problems. The glucose industry, by nature, does not appear fitted to survive.

The foregoing review and discussion, and the references appended have seemed desirable in order to coordinate the subject in outline in an accessible manner. The presentation is intended further, in avoidance of excessive complexity and length, to serve as an introduction for a paper shortly to follow, which will submit the ways and means of the new industrial maltose process which has resulted from the author's study of this special aspect of an, to him, exceedingly interesting field of industrial chemistry.

The subjoined list of references is sufficient for an introduction to the subject, in view of the excellent bibliographies, etc., contained in several of the volumes noted. For first attention, the author would venture to particularly recommend Effront's



(Prescott) "Enzymes and Their Applications," and Sadtler's "Industrial Organic Chemistry" in so far as it covers "Manufacture of Maltose."

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MILLING OF WHEAT AND TESTING OF FLOUR<sup>1</sup>

By HARRY MCCORMACK

There is one great industry which thus far has depended very little on the service of the chemist and chemical engineer in the preparation and marketing of its products. I refer to the wheat and flour milling industry.

During the year 1912, approximately 400,000,000 bushels of winter wheat valued at \$323,000,000 and 330,000,000 bushels of spring wheat valued at \$231,000,000 were produced in this country. Practically all of this wheat is marketed as such or made into flour and marketed with no particular reference to its chemical composition. No particular attention is paid to the composition of wheat which is used for seed, as the product obtained from it is sold on optical inspection rather than on chemical analysis.

The principal markets for wheat in this country are: Chicago, Minneapolis, Duluth, St. Louis, Milwaukee, Kansas City and Omaha. The rules of the Boards of Trade governing the inspection and grading of wheat received in these markets are not uniform so that a dealer in Minneapolis selling wheat to Chicago parties may have wheat of one grade in Minneapolis and find that it is wheat of another grade when it reaches Chicago. This fact has accounted for much of the difficulty encountered by grain dealers under inspection of Federal Officials seeking to enforce the Pure Food Laws.

The grading of wheat on the Chicago market may be taken as typical of the grading at all of the principal markets mentioned, as the differences are not very marked and all of them recognize the same varieties and grades of wheat, viz:

Winter Wheat, Spring Wheat, Pacific Coast Wheat and Mixed Wheat. The Winter Wheat is classified as: White Winter Wheat, under which there are four grades depending upon the weight per bushel and the percentage of other varieties of wheat present in the mixture; and the same number of grades of Red Winter Wheat and Hard Winter Wheat, depending upon the same conditions. Under the division of Spring Wheat, we have the sub-divisions: Hard Spring Wheat, Northern Spring Wheat of which there are four grades: White Spring Wheat with four grades corresponding to those under Spring Wheat, Durum Wheat of which there are four grades and Velvet Chaff Wheat of which there are four grades. The Pacific Coast Wheat is Red or White; each of these have three grades, depending as do the other wheats on the weight per bushel and the percentage of dirt and mixed varieties present with it.

The grading of this wheat, as it comes on the market, is primarily a matter of the exercise of judgment on the part of the buyer and seller. Many times their decision is at variance with that of the grain inspector or his judgment may conflict with that of either the buyer or the seller. In such a case there is no definite recourse for any of the parties concerned. The question can be decided only by the judgment of parties not interested

in the transaction, but who have no more definite basis for their opinion than have the first parties concerned.

This condition of affairs has led some of the large millers and also some of the large grain companies to seek the services of the chemist, to see if a more satisfactory basis for trading in wheat cannot be reached. The present paper aims to present some of the problems encountered in the attack on this problem and will attempt to point out some of the conditions which it will be necessary to meet before the handling of wheat on a scientific basis is possible.

Grain dealers primarily interested in the establishment of a scientific basis for buying and selling of wheat are those who really buy and sell wheat, not mere traders on the Board of Trade and, in addition to this, they are the dealers whose trade is largely with the milling interests. The miller, of course, is interested primarily in securing a wheat which will give him a satisfactory flour with as large a yield of the better grades of flour as is possible. By the term satisfactory flour, we mean a flour which corresponds in grade to the customary product of his mills and which meets the demands of his customers. It may be a so-called Hard Winter Wheat flour, a Soft Winter Wheat flour, a Hard Spring Wheat or a Soft Spring Wheat. These names are supposed to refer to the wheat from which the flour is milled, but do not always. We have many instances in which Winter Wheat flours contain no Winter Wheat and other instances in which Spring Wheat flours contain no Spring Wheat. At the same time these flours must meet in a general way the prevailing demands for color and texture, which are supposed to be characteristic of flours milled from these varieties of wheat.

A person not familiar with the variations in wheat composition may be of the opinion that wheat of the same variety, from the same locality, will not vary much in composition from season to season. This, however, is incorrect as has been shown by the work of Le Clerc and others who have studied the effect of varying climatic conditions on the same variety of wheat. Further than this it has been shown by the same investigators that the same variety of wheat grown in different localities will change very materially in composition. Taken in connection with this, it is necessary to state that a grain dealer in the largest market rarely has accurate information as to the precise origin of the sample of wheat he is purchasing. These statements indicate the necessity for a constant examination of the samples of wheat being purchased.

We must realize, at once, that the laboratory milling of a wheat cannot be done in the same manner as in the mills of the large flour manufacturers. We must then, at the outset, take into account the fact that it is impossible for us to mill experimentally a flour which can be compared directly to the flour produced in the large mill and at this point, it may be well to say that the grading and testing of flour is very largely a matter of comparison. The miller desires a wheat as has been said, which will give him his customary flour. The wheat which will do this is determined by milling it experimentally and comparing the flour produced with the flour he is producing in his mill. This will mean that if the comparison is to give any indication as to the value of the wheat in producing the desired flour, the methods of milling the wheat must be the same at all times for the same variety of wheat. Any variation in the milling will produce a variation in the flour and thus an incorrect opinion as to the value of the wheat may be deduced. This is shown very clearly in Tables A and B which give the results obtained on the same sample of wheat sent to several laboratories, these being the ones best known to the milling trade and with the highest reputation for the character of their work. These tables show, very clearly, that each laboratory has its own method of milling and to some extent its own method of testing a flour obtained by this milling. The majority of laboratories milling wheat and testing flour have approximately the same

<sup>1</sup> Presented at the 48th Meeting of the A. C. S., Rochester, September 8-12, 1913.



laboratory milling equipment, yet the way they conduct the milling differs and leads in most instances to quite different results. Table A shows the comparison of the flours produced, using a soft Winter Patent as standard. Table A1 gives the original data from which these comparisons on Table A were computed.

The milling apparatus employed in preparing the flours, the data upon which are presented in this paper, is a Standard Type of Experimental Milling Equipment and will, therefore, be described at this time.

TABLE A—COMPARATIVE FLOUR TEST REPORTS ON THE SAME WHEAT BY DIFFERENT LABORATORIES. TWO SAMPLES OF THE SAME LOT OF KANSAS No. 2 HD FURNISHED TO EACH. ALL FIGURES REFERRED TO SOFT WINTER PATENT AS 100 PER CENT PERFECT

	Armour Grain Co.		Lab. C		Lab. D		Lab. B	
Gluten, per cent. ....	9.15	9.15	9.5	9.0	9.36	9.68	9.3	9.4
Ash, per cent. ....	0.46	0.47	0.44	0.45	0.483	0.466	0.43	0.43
Absorption, per cent. ....	56.0	56.0	54.7	53.8	54.2	53.3	57.0	57.0
Color .....	100.0	100.0	100.0	100.0	94.0	93.0	92.0	92.0
Loaves per barrel. ....	102.6	102.6	100.0	99.7	100.0	100.6	100.0	100.0
Size of loaf .....	106.0	106.6	97.9	101.5	105.2	100.5	100.0	100.0
Quality of loaf. ....	102.0	102.0	...	...	100.0	100.0	98.5	98.5
Average value. ....	102.7	102.7	...	...	99.7	98.4	97.6	97.6
Ferment period. ....	100.0	100.0	...	...	111.0	111.0	101.3	101.8
Quality of gluten. ....	103.0	103.0	...	...	115.7	109.8	98.6	98.1
Per cent straight flour milled. ....	65.0	65.5	74.5	75.0	66.49	61.02	67.0	67.5

It will be noted that each laboratory except D milled on the two samples approximately the same amount of flour. The results obtained in testing the flour are fairly concordant, too, where the same amount of flour is milled. Laboratory D, with considerable variation in milling, also shows considerable variation on the values reported for certain tests.

The milling equipment consists of a special Allis-Chalmers Experimental Mill comprising three sets of six-inch rolls and a jig bolting machine. Two sets of the rolls are corrugated: one set 16 and 12 to the inch and the other 24 and 18 to the inch. These rolls grind dull to sharp and the fast roll runs a little more than twice as fast as the slow one. The smooth rolls have a differential of 7 to 10, that is, the fast roll makes 10 revolutions while the slow one makes 7. Accurate adjustment of the rolls is provided by two large screws on the side of each roll, which allow the rolls to be adjusted so that they are in the same plane,

Any successful milling of a wheat requires the very gradual reduction of the wheat to flour and it is in this gradual reduction that the experimental mill falls short of what may be accomplished with a commercial milling equipment. At the same time, the experimental milling must follow along the same lines as the commercial milling if the flour obtained is to accurately represent the flour-producing value of the wheat.

A somewhat extended line of experiments convinced us that it is necessary to decide for each variety of wheat approximately the quantity of straight flour we desire to produce from it and

TABLE A1—REPORTS ON MILLING AND BAKING TESTS ON THE SAME WHEAT BY DIFFERENT LABORATORIES. EACH SENT TWO SAMPLES OF THE LOT OF KANSAS No. 2 HD

	Armour Grain Co.		Lab. D		Lab. B		Lab. C	
Wheat protein. ....	10.9	10.7	10.6	11.0	11.01	11.33	10.9	10.8
Wheat ash. ....	1.90	1.92	1.70	1.60	1.55	1.575	1.73	1.73
Wheat moisture. ....	12.5	12.7	11.0	10.3	8.68	9.18	12.2	12.2
MILLING TEST								
Wt. wheat milled, grams. ....	1000.0	1000.0	2000.0	2000.0	985.0	975.0	800.0	800.0
Passes on rolls. ....	{ 3 Coarse 2 Medium 7 Smooth		Same		{ 6 Coarse 9 Smooth		{ 3 Coarse 12 Smooth	
Wt. of bran, grams. ....	297.0	283.0	78.0	85.0	250.0	250.0	200.0	200.0
Wt. of shorts, grams. ....	53.0	62.0	258.0	258.0	80.0	130.0	65.0	60.0
Wt. of flour, grams. ....	600.0	622.0	1490.0	1502.0	655.0	595.0	535.0	540.0
Flour protein. ....	9.15	9.15	9.5	9.0	9.33	9.37	9.3	9.4
Flour ash. ....	0.46	0.47	0.45	0.44	0.483	0.466	0.43	0.43
Flour moisture. ....	12.48	12.18	12.80	12.50	12.25	12.50	13.2	13.3
BAKING TEST								
Absorption. ....	56.0	56.0	54.7	53.8	54.2	53.3	57.0	57.0
Time of max. exp., min. ....	167.0	179.0	316.0	328.0	151.0	150.0	180.0	180.0
No. of rises. ....	2.0	2.0	...	...	4.0	4.0	3.0	3.0
Vol. of loaf, cu. in. ....	86.1	84.9	186.0	193.0	90.0	86.0	102.2	102.0
Flour per loaf, grams. ....	340.0	340.0	340.0	340.0	340.0	340.0	350.0	350.0
Wt. of loaf, grams. ....	490.0	492.0	489.0	487.0	410.0	416.0	515.0	510.0

and by two smaller screws to set them parallel. The rolls are thrown "in" and "out" by means of a lever. A mechanical jig bolting machine completes the equipment of the mill. Frames of standard bolting-cloths are made to fit this jig and as many as four frames may be inserted at one time.

Before going to the mill the wheat must be clean, as that term is ordinarily understood. This is usually accomplished by the use of some sort of fanning mill, which does not, however, remove much dirt from the crease. In these experiments a Eureka Horizontal Close Scourer was used. It removes the

then mill in such a manner as to produce the very best flour possible from the wheat and of the percentage previously determined. Different varieties of wheat are capable of producing different quantities of first class straight flour and any attempt to produce more than this percentage of flour from these wheats will at once lower the quality of the flour secured.

Our experimental work convinced us that the Northern Spring wheats gave the best straight flour when milled to produce about 66 per cent of product. Hard Winter wheats produced the best flour when milled to about 63 per cent of straight

flour. Soft Winter wheats should not be milled to produce an excess of about 38 per cent of straight flour. A more intensive milling of any of these wheats leads at once to a marked reduction in color and also to an increase in the percentage of ash, both showing that bran particles are finding their way into the flour. This is most marked on the Soft Winter wheats and the result of a too intense milling of a No. 2 Red Soft Winter Wheat is shown in Table B.

The adjustment of the rolls in the experimental mill will be determined by the size of the wheat kernels being milled. The wheat should pass through the rolls set first so that the wheat kernels will be cracked and this as lightly as possible. They

TABLE B—MILLING TESTS ON SAMPLE OF NO. 2 RED WHEAT  
Showing the Effect of Too Intense Milling

Milled to.....	65.5	58.5	Color.....	94.0	101.0
Gluten.....	9.6	9.5	Average value	95.3	98.5
Ash.....	0.43	0.37	Qual. of loaf.....	96.5	100.5

should then be brought closer and closer together until they finally run almost touching as the wheat receives its final milling on this set of rolls. After each passage through the rolls, the product goes to the sieves. Our customary arrangement of the sieve is to place at the bottom of the jig a No. 11 flour sieve, on top of this a No. 34 bran sieve and on top of this a No. 16 or No. 18 coarse bran sieve. In the first set of rolls only the product remaining on the upper sieve is remilled. When the milling has been completed on the first set of rolls, which will be accomplished in about three passes, the material remaining on both of the bran sieves is passed to the second set of rolls. About three passes on these will be sufficient. The material from both the first and second bran sieves is then weighed up and discarded from further milling operations. Up to this time, only a very small percentage of flour has been produced and has found its way from the flour sieve to the receptacle provided for it. The material remaining on the flour sieve then passes to the smooth rolls for final milling. In our laboratory, it is customary to pass the material through the smooth rolls eight times, with sieving between each passage and with the space between the smooth rolls being made smaller and smaller. Practically all of the flour is produced in this milling on the smooth rolls. The material remaining on the flour sieve after this milling is weighed up and discarded. The material which has passed through the flour sieve is resifted through a No. 13 flour sieve to remove some of the bran particles and dirt which may have escaped the No. 11 sieve and is weighed to give the percentage of flour produced. The flour produced in this way should be very uniform in texture and color, and should be entirely free from any specks of bran or dirt.

The flour thus produced will compare very favorably with the straight flour produced in any commercial mill. It will, of course, not be equal to the patent flour marketed from a commercial mill, as this patent flour is made by taking the straight flour milled and by subjecting it to a system of air separation and sieving to remove much of the bran particles and some of the germ, which otherwise find their way into the straight flour. The patent flour will vary with different mills and brands all the way from 45 per cent to 90 per cent of the straight flour milled.

The milling description, which has been given, applies to wheats which have recently been harvested and which contain their normal moisture content. In case the wheat has been harvested for some months and has lost a considerable percentage of its normal moisture, it is necessary to add water to the wheat and allow this water to be taken up by the wheat before milling. This process is known as tempering and is for the purpose of softening the bran layers so that they will flatten out in the rolls instead of cutting up.

The methods of milling are stated because they are the ones

we found best and not because we believe it is impossible to improve on them. These methods are suggested for use until better ones are devised and until the various laboratories can agree on a common method of milling.

At present each laboratory is a law unto itself in its methods of milling. They are like us, they know their methods are best and have no use for the methods used in any other place. Many of them seem to think the milling of wheat is a secret process and thus instead of disclosing in their reports the methods of milling employed in producing a flour, the testing of which is covered in report, the report is formulated in such a way as to conceal as much of the process as is possible.

This led us to send out some samples of wheat to certain laboratories, these samples being accompanied by a data sheet such as we desired filled out. Most of the laboratories supplied the data requested, but from some of them we were never able to secure statements covering their methods of operation which were complete enough to enable us to make an intelligent comparison between their methods and results and the methods and results as obtained by ourselves and others. The data we were able to secure is shown on Tables A2 to A5 inclusive.

TABLE A2—COMPARISON OF REPORTS ON THE SAME LOT OF WHEAT BY DIFFERENT LABORATORIES

No. 2 Spring Wheat	Milling, Baking and Chemical Data			
	Armour Grain Co.	Lab. A	Lab. C	Lab. B
Wheat protein.....	14.3	.....	13.1	13.8
Wheat ash.....	1.87	.....	1.8	1.88
Wheat moisture.....	12.1	.....	11.2	12.2
MILLING TEST				
Wt. wheat milled, grams.....	1000.0		2000.0	800.0
Passes on rolls.....	3 Coarse			
	2 Medium			3 Coarse
	7 Smooth			12 Smooth
Wt. of bran, grams.....	297.0	.....	93.0	200.0
Wt. of shorts, grams.....	53.0	.....	298.0	65.0
Wt. of flour, grams.....	632.0	.....	1487.0	535.0
Flour protein.....	12.75	.....	12.6	12.3
Flour ash.....	0.49	.....	0.50	0.45
Flour moisture.....	11.56	.....	12.7	13.1
BAKING TESTS				
Absorption.....	56.0	67.0	56.8	61.0
Time of max. exp., min.....	181.0	125.0	310.0	205.0
No. of rises.....	2.0	.....	.....	3.0
Vol. of loaf, cu. in.....	88.2	38.0	203.0	109.0
Flour per loaf, grams.....	340.0	100.0	340.0	350.0
Wt. of loaf.....	494.0	.....	494.0	515.0

It is our opinion that most of the variations shown throughout this data sheet are due to variations in milling, as when we sent out flour samples for comparative tests the results were more concordant.

The determinations made in the chemical analysis of the flour are: ash, moisture, total nitrogen, and on some samples gliadin nitrogen.

These determinations were made in the customary way. It is, therefore, unnecessary to describe them further than the following comments:

Ash can best be determined in an electrically heated muffle furnace, first at a low temperature, then increasing to a full red heat.

Moisture can best be determined using a glass tube to contain the sample: a tube about  $\frac{1}{2} \times 3$  inches is used and placed in the oven horizontally. After drying it must be weighed in a telescopic weighing tube as it is highly hygroscopic.

Some trouble was experienced in the distillation for the nitrogen determination when a certain type of safety bulb tube was used. Some of the alkaline liquor was invariably carried over; it is recommended, therefore, that only the form known as the Hopkins safety bulb tube be used.

These determinations are made use of in the valuation of a flour about as follows: the ash tells us in a rough way about

how much of the bran has found its way into the straight flour milled, as the patent flours have the lowest ash of any on the market. The patent flours made from the different varieties of wheat have somewhat nearly a constant ash and by comparing the ash of our straight flours with those of the patent flours obtained from corresponding varieties of wheat, we have a measure of the value of a wheat which is being tested for its production of patent flour.

The moisture determination is used in calculating all of the

TABLE A3—COMPARISON OF REPORTS ON THE SAME LOT OF WHEAT BY DIFFERENT LABORATORIES

No. 2 Red Wheat	Milling, Baking and Chemical Data			
	Armour Grain Co.	Lab. A	Lab. D	Lab. B
Wheat protein .....	11.5	11.33	11.30	
Wheat ash .....	1.93	1.55	1.82	
Wheat moisture .....	10.7	8.45	11.8	
MILLING TEST				
Wt. wheat milled, grams.....	1000.0	975.0	800.0	
Passes on rolls .....	<div> <div>3 Coarse</div> <div>2 Medium</div> <div>6 Smooth</div> </div>	<div>6 Coarse</div> <div>10 Smooth</div>	<div>3 Coarse</div> <div>11 Smooth</div>	
Wt. of bran, grams.....	307.0	290.0	195.0	
Wt. of shorts, grams.....	47.0	80.0	70.0	
Wt. of flour, grams .....	606.0	605.0	535.0	
Flour protein .....	9.58	9.41	9.6	
Flour ash .....	0.47	0.45	0.39	
Flour moisture .....	11.32	12.25	12.65	
BAKING TEST				
Absorption .....	54.5	62.0	51.6	57.0
Time of max. exp., min.....	174.0	113.0	14.0	150.0
No. of rises .....	1.0	4.0	3.0	
Vol. of loaf, cu. in.....	78.5	34.5	96.0	102.2
Flour per loaf, grams.....	340.0	100.0	340.0	350.0
Wt. of loaf.....	492.0	415.0	510.0	

TABLE A4—COMPARISON OF REPORTS ON THE SAME LOT OF WHEAT BY DIFFERENT LABORATORIES

No. 2 Spring Wheat	Spring Patent as Standard			
	Armour Grain Co.	Lab. A	Lab. C	Lab. B
Gluten, per cent.....	12.75	12.6	12.3	
Ash, per cent.....	0.45	0.50	0.45	
Absorption, per cent.....	56.0	67.0	56.8	61.0
Color.....	100.0	87.0	98.0	98.0
Loaves per bbl.....	95.0	101.8	101.0	99.4
Size of loaf.....	100.0	100.0	100.0	
Quality of loaf.....	100.0	90.0	98.5	
Average value.....	98.7	97.7	97.7	
Fermenting period.....	100.0	103.6		
Quality of gluten.....	100.0	96.6		
Per cent straight flour milled.....	65.0	74.3	67.0	

TABLE A5—COMPARISON OF REPORTS ON THE SAME LOT OF WHEAT BY DIFFERENT LABORATORIES

No. 2 Red Wheat	Armour Grain Co.			
	Lab. A	Lab. D	Lab. B	
Gluten, per cent.....	9.58	9.68	9.60	
Ash, per cent.....	0.47	0.45	0.39	
Absorption, per cent.....	54.5	62.0	51.6	57.0
Color.....	102.0	95.0	95.5	94.0
Loaves per barrel.....	100.0	98.3	99.6	100.0
Size of loaf.....	99.0	90.7	112.4	100.0
Quality of loaf.....	101.2	97.0	100.0	99.0
Average value.....	100.5	95.4	101.6	98.2
Fermenting period.....	100.0	132.8	111.0	102.7
Quality of gluten.....	98.5	89.3	109.8	97.4
Per cent straight flour milled.....	65.0	45.0	62.05	67.0

samples tested to a constant basis of moisture content. It is also used in calculating the quantity of water absorbed by the flour in the preparation of a dough of standard consistency.

The nitrogen determination is on the same basis as the ash determination. It is a comparison between the nitrogen of the straight flour and that of the patent flour prepared from the same varieties of wheat. As the nitrogen on the whole wheat is higher than in either the straight flour or the patent flour

prepared from it, the value of the wheat as a source of patent flour varies inversely as the ratio between nitrogen in straight flour and nitrogen in patent flour.

The determination of gliadin nitrogen is made in order to compute the ratio between total nitrogen and gliadin nitrogen. In general, the higher this ratio the higher is the quantity of the flour. Whole wheat flours have the lowest gliadin number and there is a constantly increasing ratio from the whole wheat up to the patent flour. Some determinations of total nitrogen, gliadin nitrogen and the gliadin numbers are shown in Table C.

The testing of the flour for its bread-producing qualities is carried out in all of the laboratories in about the same way and, as previously stated, there is not much difficulty in getting concordant results from different laboratories working on the same sample of flour.

The determinations made in the baking test are absorption, color, the size of the loaf, the texture of the loaf and fermenting period, and from these determinations are calculated the loaves per barrel, the average value of the flour and the quality of the gluten. The absorption is expressed as the quantity of water necessary to add to a hundred parts of flour to make a dough of standard stiffness. The other figures are comparative using the standard flour as 100 per cent on each of the items mentioned.

There are two general types of dough-handling adapted to the baking of tinned bread. These are generally known as the "sponge" method and the "straight dough" method.

In the sponge method somewhat less than one-half of the flour is mixed with an equal weight of water and all other ingredients. It is then allowed to ferment for 1½ to 2 hours, depending on the type of flour, and is then mixed with the remainder of the flour and water to make a dough of the proper consistency. It is then allowed to rise twice and is formed into loaves, placed in the pan in which it is to be baked, and allowed to rise a definite amount. It is then baked. The complete operation takes about 4½ hours.

The straight dough method is in general the same as the sponge method with the omission of the sponging stage. In other words

TABLE C—PROTEIN AND GLIADIN DETERMINATIONS WITH CALCULATED GLIADIN NUMBERS

Description of wheat from which flour is made	Protein	Gliadin	Gliadin No.
No. 1 HARD SPRING			
1102	11.2	6.62	59.1
1108	11.3	6.70	59.3
No. 1 VELVET CHAFF			
1103	11.4	6.97	61.1
1109	11.6	6.90	59.5
No. 1 BLUE STEM			
1104	11.8	6.92	58.6
1111	11.9	6.92	58.1
DULUTH No. 1 NORTH			
1105	11.3	6.92	61.2
1107	11.7	6.87	59.7
No. 1 HARD SPRING			
1106	11.6	6.95	60.0
1110	11.8	7.07	60.0
SPRING PAT. (purchased)	10.8	7.40	68.5

the dough is mixed to the proper consistency for baking at the very start of operations instead of after a sponging stage. This naturally subtracts the time of sponging from the operation and enables a far larger number of samples to be handled.

In fact, with the same equipment, it has been found that just double the number of samples can be handled in one 8-hour day if the straight dough method is used instead of the sponge method. The quality of the loaves will be uniformly slightly lower, but the results being comparative with each other, this cannot affect the test.

For the above very potent reasons, the straight dough method is used in our laboratory.



## THE BAKING TEST

**METHOD**—A modification of the baking tests as outlined in *Bulletin 117* of the Kansas State Agricultural College was used, because several things were thought necessary to bring the test into such form that its results would more closely give the actual commercial value of the flour.

For instance it was found that some flours from the red wheats of the southern states could not be baked satisfactorily by the above original method, whereas they are used to good results in practice. The modification that follows gives very good loaves.

In making baking tests on different flours it is above all desirable that the test should be so conducted that the differences in the results should be caused by the inherent qualities of the flour and not by variations due to the method employed. However, in practice the skilled baker adapts his method to suit the different flours he uses, and he remedies the defects in the flour so some extent by the method of baking he uses. Therefore it has been the writer's aim to conduct these tests in such a way as to get as good bread as possible from the different flours, and if necessary to vary the method of baking in some slight details to be able to do this. That such a method will yield results that more closely approximate the results the flour is going to give in actual use is apparent.

The actual baking and its associated tests were made as follows:

**THE STRAIGHT DOUGH TEST**—In these tests "dough" means a flour mixture that has been subjected to a short period of fermentation and baked as soon as the dough has risen a standard amount. This amount is fixed by preliminary trial and is uniform in all these tests. The short period of fermentation varies from 1 to 3 hours and is secured by using fresh yeast in large quantities.

Before making the dough we must know the percentage of water that the flour will absorb to be of correct stiffness. This is found by weighing out 30 grams of the flour into a strong teacup and running in distilled water from a burette until the resultant dough is "right." The best test that the dough is "right" is to put it on the bottom of the cup in the form of a round ball and watch it for about 3 minutes. If it gradually settles down until it touches the rim of the circle on the bottom of the cup it is satisfactory. If it stays in the original shape it is too stiff, whereas if it quickly subsides and overlaps the edge of the cup it is too thin. This test will be found to be sensitive in careful hands to within  $\frac{1}{4}$  cc. on 30 grams of flour. The water that the flour absorbs is figured in percentage.

Now the dough can be made: 340 grams of flour, 10 grams of sugar, and 5 grams of salt are weighed out. The amount of water as determined by the absorption test, less 50 cc., is also measured out. The flour is placed in the pan in which it is to be baked and placed in the constant temperature oven until it reaches  $35^{\circ}\text{C}$ . As many grams of yeast as are necessary for the whole batch of loaves are weighed out and dissolved in enough cold water to just be able to draw out 50 cc. of the resultant solution for each batch of dough: 10 grams of yeast should in this way get into each batch of dough.

When the flour is warmed to the right temperature it is removed from the oven and two-thirds of it is placed in a dish. The water as measured out is heated to  $42^{\circ}\text{C}$ . and the sugar and salt dissolved in it. Then exactly 50 cc. of the yeast solution are withdrawn in a pipette and added to the sugar and salt solution. The temperature of the resulting mixture should be very close to  $35^{\circ}\text{C}$ . This liquid mixture is then added to the flour. The resultant batter is beaten up with a large spoon or spatula until there are no more lumps, which usually takes about 2 minutes. The remainder of the flour is then added and the dough mixed, first by means of spatulas and then the hands, to a ball of well kneaded consistency. After this operation, which usually takes but two or three minutes, the dough is placed back in its pan, which has been buttered in the meantime, and put back

in the rising oven where it is kept at  $35^{\circ}\text{C}$ . The dough is weighed at this time to ascertain the loss during the kneading. This loss is unavoidable, and usually is about 15 grams. It is due mostly to evaporation of moisture and sticking of some dough to the hands.

The dough is now allowed to rise the standard amount and if it is a very weak flour from a soft wheat, it is immediately baked, but if the flour has any reasonable strength it is knocked down, reknaded, and allowed to rise a second time, and at the termination of this rise if the dough of one of the loaves shows signs of collapsing that loaf is then baked, otherwise a third rise is used. Most flours coming from sound wheats will stand three rises; they will even need them. The times of rising are carefully noted, and all loaves are baked exactly 30 minutes at  $238^{\circ}\text{C}$ . About  $\frac{1}{2}$  to  $\frac{3}{4}$  of an hour after the loaf has been standing in the open air, it is weighed, and this weight is recorded as the weight of the hot loaf. This must, of course, be corrected for the small amount of dough lost in the kneading.

In measuring the volume of the loaf it is put in an oblong box that already contains some turnip seed. Then the box is filled with the seed, gently rapped, and the seed leveled off at the top. The seed is poured out and weighed, and from the weight of seed that the box will contain when there is nothing but seed in it, the volume of the loaf can be obtained, since the volume of the box is known. This method has been found to be accurate to within 5 grams of seed, which correspond to about 2-5 cu. in. in volume.

The volume should be measured approximately one hour after removing the loaf from the oven as it will shrink more and more the longer it stands.

## GLUTEN EXPANSION DOUGH TEST

This is for the purpose of testing the quality of the gluten and checking the relative fermentation period of the flour. The procedure is identical with that for the straight dough except that 100 grams of flour are used instead of 340 grams, and the other ingredients in proportionate amounts. At the point where the regular dough would be panned, this dough is placed in the bottom of a well greased glass cylinder which is at a temperature of  $35^{\circ}\text{C}$ . and placed in the rising oven at  $35^{\circ}\text{C}$ .

For the first hour no attention is required, but after that the height of the dough and the time should be recorded every 15 minutes; and later when it is evident that the dough is near its maximum volume, every five minutes. When the dough just begins to fall the volume and time are noted. From the difference in initial and final volumes the relative qualities of the glutes are calculated. Since we start with the same amount of flour, the quality of the gluten itself will be equal to the net rise divided by the per cent gluten in the sample. This figure is then referred to the similar figure of the standard flour on a percentage basis.

Another method of performing this test which seems to yield more definite results uses the gluten itself instead of the dough. For this purpose the gluten is washed out of the flour in the usual way, and then 10 grams of each gluten are placed, wet, in a tin cylinder 1 inch in diameter and placed in the bake oven at  $200^{\circ}\text{C}$ . It will be found that the gluten will expand and after twenty-five minutes will have formed a porous column within the tin. The height of this column will be directly proportional to the quality of the gluten.

In making all these tests, there is selected and tested at the same time a flour, the baking qualities of which are known. The results are compared on a percentage basis and in this way the unknown flour is judged.

We are led from our laboratory experience to make the suggestion that some form of mechanical kneading apparatus which can be kept at constant temperature should be used in all of the kneading operations. If this is not done, there is considerable chance for variation in the results obtained for

fermenting period, texture and size of loaf. We also suggest that the color be determined on the samples of flour rather than on the bread and that this color be determined with an instrument such as the Lovibond tintometer and that it be expressed in the number of standard color used rather than by any percentage system which may be based on the standard flour. At present there seems to be a different method of expressing color in use by each laboratory engaged in flour testing.

We may sum up the results we have been able to obtain in our experimental work on the milling of wheat and testing of flour by saying that we are able to secure results which are satisfactory to us in showing the flour-producing qualities of any wheat. We shall qualify this statement by saying that, at the present time, it is very difficult to express our results in such a way that they will convey an adequate understanding of these results to other parties such as millers or flour jobbers.

The primary object of this paper is to present the need for uniform methods to be employed in the milling and testing operations and a uniform method of expressing the results obtained so that any party receiving a report from any laboratory on any particular wheat or flour, will be able to read this report intelligently and to compare it with any other report which he may receive from this or any other laboratory on the same sample of wheat. It is impossible to interest the millers, or to any considerable extent the grain dealers, in the testing of wheat and flour, until they are able to obtain concordant and satisfactory reports on any sample which they may submit.

The first move in the satisfactory solution of this question must be made by the chemist and the chemical laboratories who

are seeking the trade of the grain dealer and the miller. The importance of this work may be inferred to some extent by stating that on single days in the past year one firm of grain dealers disposed of, to millers, more than 200,000 bushels of wheat.

Another factor which enters into the importance of such work is that in many years the wheat crops of certain localities are short, while an abundance of wheat of a different variety may be obtainable from other sections. This is very well illustrated by the conditions of the past year, when the winter wheat crop throughout the country was unusually low. Millers using quantities of Winter Wheat in their milling mixture had to pay a considerable premium above the normal price of wheat to secure varieties of wheat they desired. In some instances this premium amounted to 16 cents per bushel or \$160.00 per car. Substitutes for the desired varieties of wheat were consequently in demand and these substitutes also brought a considerable premium in price, ranging from 8 to 16 cents per bushel.

You will note, therefore, that any grain company, which by the service of its chemist may be able to pick up any quantity of these wheats so much desired by the millers will thus make a handsome profit above the expense connected with the operation of a laboratory.

The extension of the wheat and flour testing will undoubtedly be determined by: (1) The ability of the chemists to agree upon a uniform method for conducting the testing and in expressing their results; (2) The ability of the chemists to convince the grain dealer and the miller of the profit which may be derived from a satisfactory knowledge of the wheat being purchased.

ARMOUR INSTITUTE OF TECHNOLOGY LABORATORIES  
CHICAGO

## CURRENT INDUSTRIAL NEWS

By M. L. HAMLIN

### FULLER'S EARTH

According to official figures as given in the Oil, Paint and Drug annual report, the value of Fuller's earth produced in the United States in 1912 was \$305,522, and Florida was the leading producing State. The principal use of Fuller's earth in this country is in the bleaching, clarifying or filtering of fats, grease and oils. The market for Fuller's earth was quiet, but steady through the year, and prices varied according to quality. Imports of Fuller's earth for the fiscal year with comparisons were:

	Tons	Values
1913.....	16,866	\$145,588
1912.....	16,175	138,111
1911.....	15,813	125,899
1910.....	13,192	118,956
1909.....	11,489	100,269

### FINANCIAL AND LABOR CONDITIONS ON ENGLISH RAILROADS

In an editorial comment on the railway situation, during the past year in England, *Engineering* (London), 97 (1914), 322, publishes the following:

"The past year has, on the whole, been a very prosperous one for the railways, but the gross increases have, to a very large extent, been swallowed in additional charges. The London and North-Western Railway Company, for example, has had a record year: the net receipts amounted to \$30,722,786, which is an increase of \$4,525,000. Expenses, however, increased by \$3,472,600, of which a very large fraction is attributable to increased wages. The Great Western Railway Company's receipts again showed an increase of \$5,194,350 on the year. At the same time charged increases by \$3,482,300. These figures may be taken as fairly typical. The increased

wages cost is, of course, not wholly due to increased rates of pay or shorter hours, but in part to the necessity of employing additional hands to meet the necessities of the exceptional traffic. Such additional labor is necessarily somewhat inefficient, and a feeling of good comradeship also has its effect in inducing the old hands to slack off a little, so as to avoid the risk of "working the new men out of a job." In the case of the London and North-Western Company, for example, of the two and one-half million dollars total increase in the pay bill, only one and one-half million was due to the extra rates of pay. The companies have, of course, to pay, in addition, insurance charges, which in the case of the London and North-Western line were equivalent to nearly 1 per cent on the net receipts. The total wages bill is equivalent to about one-fourth the gross receipts. The 4 per cent increase in rates demanded by the railway companies is claimed to be very far from meeting the increased wages cost.

"The very large amount of capital which must be ventured to provide employment for one railwayman is truly remarkable—averaging about \$10,000 per head. This is, of course, out of all proportion greater than in other large industries, and the tendency is for it to increase. In the shipbuilding industry the capital risked per workman amounts to no more than \$900, according to an estimate made by Dr. J. Inglis.

"One of the great problems of the day is the arrangement of some reasonable *modus vivendi* with labor. Notices for the termination of the existing agreement as to conciliation boards have been handed in pretty generally. To no small extent the difficulty with labor resides in the circumstance that while the men demand more wages, the capital for necessary extensions and developments can only be obtained if these wages are actually earned. The men, however, in many cases object to the adoption of the only means by which this desideratum can be attained, since every improvement in operating methods devised by the

administration of a railway line, by enabling more work to be done per head, checks temporarily rates of promotion. Hitherto, undoubtedly, there has been somewhat too great a tendency to substitute regulations for explanations, and to adopt generally the attitude of the Roman centurion. Direct access to officers or directors with powers of initiative may do much to make matters work more smoothly, and many of the companies are proceeding on these lines. On the Great Eastern Railway, for example, the company is represented on the Conciliation Board by a special director, and a somewhat similar policy is being pursued by other lines. Much of the trouble experienced in the past has been due to a feeling on the part of the men that the companies were evading the terms of various awards. It will be the business of these special diplomatists to remove such apprehensions before matters come to a crisis."

### IMPORTS OF SPERM OIL DURING 1913

According to the Oil, Paint and Drug annual report the importations of sperm oil during 1913 were as follows:

Date	Vessel	Barrels
April 28	Hyanthes.....	150
May 25	Richard W. Clark.....	4,150
June 1	Bark Alice Knowles.....	650
June 29	Brig Daisy.....	375
July 14	Schr. Ellen A. Swift.....	450
August 8	Schr. A. W. Nicholson.....	550
August 9	Bark Chas. W. Morgan.....	1,200
August 15	Schr. John R. Manta.....	200
September 4	Bark Gay Head.....	900
October 25	Schr. E. R. Smith.....	4,555
November 13	Schr. Richard W. Clark.....	4,425
November 13	Str. Berlin.....	1,485
Total.....		19,090

NOTE—On December 31st, the stocks of unsold sperm oil in New Bedford amounted to 1,100 barrels.

### POTASH SHIPMENTS DURING 1914

Consul-General R. P. Skinner, Berlin, Germany, states that the executive authorities of the German Potash Syndicate have resolved to authorize the following deliveries for domestic and foreign consumption during the year 1914 in accordance with the provisions of the potash-syndicate law (the amounts being in metric tons of pure potash,  $K_2O$ ):

	For domestic consumption Metric tons	For foreign consumption Metric tons
Carnallite with at least 9 per cent and less than 12 per cent $K_2O$ .....	7,100	100
Raw salts with 12 to 15 per cent $K_2O$ .....	339,000	141,100
Fertilizer salts with 20 to 22 per cent $K_2O$ .....	2,300	48,300
Fertilizer salts with 30 to 32 per cent $K_2O$ .....	4,000	16,000
Fertilizer salts with 40 to 42 per cent $K_2O$ , including potash fertilizer with 38 per cent $K_2O$ .....	211,300	67,000
Chloride of potash.....	69,700	187,500
Sulfate of potash with more than 42 per cent $K_2O$ .....	1,700	55,000
Sulfate of potash-magnesia.....	200	15,000
Total.....	635,300	531,300
Grand total.....		1,166,600

### BY-PRODUCT PRODUCERS IN GERMANY

Several German companies have had in operation for some time by-product producer-gas power plants built according to a system invented by an Englishman, A. H. Lymn. *The Journal of Gas Lighting and Water Supply*, 97 (1914), 715, says:

"A large plant on this principle has been in operation with

highly successful results for three years at the works of the Zellstoff-fabrik Waldhof, Mannheim (a Company having a capital of from \$15,000,000 to \$20,000,000) and another plant on Mr. Lymn's system has been built by his German licensees, Messrs. Ehrhardt and Schner, for the Badische Anilin- und Soda-Fabrik of Ludwigshafen-Rhein—probably the largest chemical works in the world. It is interesting for us to be able to add that Mr. Lymn's new and improved system has now been adopted by the German Government for their central power station at Heinitz. This plant is at first being constructed for 3000 K.W., but it is intended to double it later on. It will supply gas to large engines built by Messrs. Ehrhardt and Schner."

### GERMAN FOREIGN TRADE IN IRON

In the year 1913 Germany's foreign trade in iron, like her foreign trade as a whole, showed a considerable increase. *Technik und Wirtschaft*, 7 (1914), 213, gives the following data:

	EXPORTS	
	1912	1913
Iron and iron products.....	\$296,450,000	\$334,800,000
Machinery.....	157,575,000	169,600,000
Totals.....	\$454,025,000	\$504,400,000
	IMPORTS	
	1912	1913
Iron and iron products.....	\$27,550,000	\$26,025,000
Machinery.....	19,250,000	20,225,000
Totals.....	\$46,800,000	\$46,250,000

In weight, the iron exports, exclusive of machinery, reached the figure of 6,500,000 tons, while the total output of iron in Germany and Luxemburg was 19,100,000 tons (metric). The amount exported was 7.5 per cent more than in 1912, but the value of the exports showed an increase of 13 per cent. The reason for this is that the exportation of the cheaper forms of iron fell off

### EXPORTS OF IRON AND IRON PRODUCTS

Year	Metric tons
1911.....	5,380,000
1912.....	6,042,000
1913.....	6,497,000

in 1913, while that of finished products increased 15 to 17 per cent. The proportion of raw iron to the total iron export was 13.2 per cent and shows a condition similar to that in Great Britain, where the proportion of raw iron to the total iron exported sank from 25.7 per cent in 1912 to 22.2 per cent in 1913.

In the following table Germany's iron imports and exports for the last two years are classified in four groups; it will be seen here that the amount of machinery exported is seven times as great as that imported, a great increase over 1900, when the exports were only two and a half times the imports.

	IMPORTS		EXPORTS	
	1912	1913	1912	1913
Raw iron, scrap, etc. (metric tons)	493,000	451,000	1,911,000	1,754,000
Rolling mills' products.....	118,000	125,000	3,304,000	3,801,000
Machinery.....	78,000	88,000	537,000	594,000
Other products.....	\$3,000	42,000	806,000	943,000

It is noteworthy that the exports to Great Britain, British East Indies, East Asia and South America have more than made up for the falling off of the exports to other European countries; even the small amount exported to the United States was doubled. The following table shows the destinations and amounts of the greater part of the iron exported:

	1910	1912	1913
Great Britain.....	910,000	1,024,000	1,208,000
Belgium.....	753,000	798,000	648,000
Netherlands.....	386,000	555,000	595,000
Brazil and Argentine Republic.....	395,000	381,000	471,000
Switzerland.....	262,000	356,000	333,000



### NATURAL GAS IN CANADA

Remarkable progress is reported for 1913 by the Canadian Western Natural Gas, Light, Heat and Power Co. According to the *Journal of Gas Lighting and Water Supply*, 97 (1914), 639, the daily consumption amounts to some 26,000,000 cu. ft., which is paid for at the rate of 15 cents per 1000. The distribution has a capacity of 33,000,000 cu. ft. daily, but enlargements are in contemplation, since 500 consumers are being added monthly. The pressure in the borings is over 600 lbs. per sq. in., and this is practically as great as when the well was first started. It may, therefore, be assumed that the supply will last for some years. The total capital of the company at the end of 1913 amounted to more than \$9,747,000.

### TAR AND BENZOL PRICES

The *Journal of Gas Lighting and Water Supply*, 97 (1914), 640, quotes an article in the *Journal für Gasbeleuchtung*, in which appears a diagram (drawn up by Professor Dr. Ost) showing the remarkable fluctuations in the prices of tar and benzol between the years 1880 and 1905. The price of a ton of tar in 1880 was about 30 marks; in 1883 it had risen to 55; in 1887 it was down to about 16; in 1892 it was up to 40 again; from 1889 to 1905 it was round about 20 marks. The variations in the benzol curve are even more remarkable. Between 1885 and 1886 the price of 100 kg. dropped from 400 marks to 40, owing to the advent of benzol washing in coke-oven practice. In 1890 it again rose to 110 marks; in 1895 it was below 27; and in the next year it shot up to 75 again. From 1899 to 1905 it was fairly steady round about 20 marks. The prices in the London market last week were about 32 marks per ton of tar, and 27 to 28 marks per 100 kg. for benzol.

### DOMESTIC LIGHTING FIFTY YEARS AGO

The *Journal of Gas Lighting and Water Supply*, 97 (1914), 516, quotes the following paragraph from *The Builder* for Feb. 20, 1864:

"Of late, in provincial towns, and even in some villages, gas-lights have been introduced into the dwellings of the working classes—a practice which adds to the cheerfulness of homes and is not more expensive than candles. In Manchester most new houses, of even the third class, have gas-pipes laid on at the time of building. In London this is not so generally done, even in new houses of this class; and to lay the pipes to old ones, by re-opening the pavements, is a seldom recurring art. Of late, however, lamps constructed for the use of paraffin or petroleum and colza oils are coming much into use in the houses of the working classes; and it is stated that in the longest days of winter, when light is needed from between four and five o'clock p.m. till between ten and eleven, and also in the morning, the cost is only about 8d. a week. Common candles would come to about a shilling, while the paraffin gives three or four times the volume of light that could be obtained from candles for that money."

### GASES IN IRON AND STEEL

An investigation by W. Herwig, *Stahl und Eisen*, 33, 1721, on the gas contained in blisters formed on steel plates during rolling and annealing is quoted in the *Journal of Gas Lighting and Water Supply*, 97 (1914), 502. This gas consists chiefly of nitrogen. The gases evolved during the solidification of iron immediately after tapping from the blast-furnace include large quantities of hydrogen and carbon monoxide; white iron contains more hydrogen, and hot-blast gray iron more carbon monoxide. By heating in a current of hydrogen, the nitrogen in steel turnings was reduced from 0.022 to 0.006 per cent; and, though it was not increased by heating in a current of nitrogen, yet from a mixture of nitrogen and hydrogen in equal proportions a steel was obtained, in one case with as much as 0.052 per cent of nitrogen. The author considered that similar action takes

place in the converter. A steel containing 0.04 per cent of nitrogen, when tested, broke without elongation, but was improved by prolonged annealing.

### THE CINEMATOGRAPH IN RESEARCH

In an extremely interesting lecture before the Fränkisch-Oberpfälzischer Section of the Verein deutscher Ingenieure [*Zeitschrift des Ver. deut. Ing.*, 58 (1914), 268], Dr.-Ing. Hanz Goetz outlined the part cinematography had played in scientific and technical research and suggested some of the things that may be expected of it in the future. After an introduction giving statistics, describing apparatus and outlining the history of the invention, the lecture takes up the position of moving picture photography among the means of reproducing phenomena to the census. It differs from other means in that it correlates two of the basic quantities that physics deals with, time and extension in space.

The most obvious way in which the cinematograph may act as an aid to science is in recording rare phenomena such as scenes in the life of seldom seen or difficultly accessible animals, unusual surgical operations, etc.—fields in which considerable success has been attained. Its usefulness only begins here, however. Just as the scale of objects may be varied when they are represented graphically, so the time scale of actions may be changed when they are represented by the cinematograph. By an increase in speed, Professor Pfeffer, of Leipzig, has been able to reproduce in three minutes a ten-day period of growth of a horse-chestnut twig; pictures for this reproduction were taken at five minute intervals. A large field for the study of the growth of both plants and animals is thus opened up. Just as slow motions can be hastened so that it is possible to see the total effect in a truer perspective, so it is possible to retard and analyze quick movements, and the limits are only those of the speed with which the pictures can be taken. With the most refined mechanical devices it is not possible to take more than 250 pictures per second, but by illuminating the moving object with regularly succeeding electric sparks and photographing on a film moving continuously rather than intermittently, it was found possible to increase the number of exposures to 2000 per second. Bull has studied the flight of insects in this manner.

From an engineering point of view the cinematograph has been most useful in studying projectiles and their effect on armor plate. Much higher frequencies had to be used than Bull obtained, and the apparatus employed differed from his in not using a mechanical interrupter; in series with the illuminating spark-gap was a large condenser, and in parallel with it a small one; the large condenser is charged by an induction machine, and when it is discharged the small condenser is alternately charged and discharged across the gap. The period of the alternations can be judged with fair accuracy by the tone. Since an explosion can take place in the five-thousandth part of a second, the speed of nine to fifty thousand exposures per second, obtained by this method, is sufficient to furnish interesting results. Since it is obviously impossible to have the camera near the object photographed, a special arrangement is used.

The cinematograph can also be used for making quantitative measurements of movements. The fall of a body has been studied by photographing on the same film the falling object and the hand of a chronograph, and in the same way the action of a steam hammer has been timed.

In these lines the cinematograph has just begun to be developed, and offers great possibilities in solving problems dealing with time and space in fields as wide apart as engineering and biology, and makes possible the study of motions so slow that it has hitherto been impossible to form conception of their whole meaning, or so fast that it has been almost impossible to form any conception of them at all.

## CHEMICAL INDUSTRIES IN JAPAN SINCE 1911

Japan's foreign trade has increased considerably in the last year. Imports in 1912 amounted to \$318,000,000, in 1913 to \$372,000,000; exports in 1912 amounted to \$269,000,000, and in 1913 to \$321,000,000. Chemical trade has in general shared in this increase, though the establishment of several factories in Japan, financed chiefly by foreign capital, has greatly cut down the importation of some substances such as formalin and acetic and salicylic acids. On January 1, 1911, there were, in Japan, 470 factories producing chemicals or related products; of these 159 manufactured explosives, 83 oils and waxes, 77 pharmaceutical products, 21 rubber, 13 toilet preparations, 30 soaps, 5 dyes, 49 fertilizers, and 33 were unclassified in the official statistics. Germany and England have furnished the larger part of the imports, but in the last three years American competition has made itself keenly felt.

The *Chemiker-Zeitung*, in which appear the above data, publishes also, 38 (1914), 395, the following table of chemical imports for 1911 and 1912:

	1911	1912
Acids: Boric.....	\$ 49,150	61,000
Citric.....	15,550	20,000
Acetic.....	5,400	3,450
Carbolic.....	69,500	135,000
Salicylic.....	101,400	53,850
Tartaric.....	24,150	42,700
Alum.....	5,650	400
Ammonium carbonate.....	34,250	45,900
Ammonium chloride.....	.....	45,950
Anilin salts.....	25,100	71,550
Antifebrin.....	20,450	19,450
Antipyrine.....	84,550	86,100
Bismuth nitrate.....	177,150	83,300
Calcium acetate.....	.....	146,000
Camphor, borneol, etc.....	41,750	16,350
Cocaine salts.....	39,750	82,250
Explosives: Dynamite.....	328,750	380,050
Detonators.....	71,900	42,650
Other explosives.....	20,150	50,450
Formalin.....	112,550	59,550
Gelatin.....	32,950	37,350
Glycerine.....	408,100	393,300

	1911	1912
Guaiaacal carbonate.....	.....	66,400
Glue.....	156,450	191,100
Magnesium carbonate.....	8,750	9,150
Milk sugar.....	28,450	34,050
Morphine salts.....	49,550	73,850
Phosphorus, yellow.....	97,800	132,500
Phosphorus, red.....	185,350	187,600
Potassium chlorate.....	620,100	650,100
Potassium bichromate.....	49,450	125,700
Potassium bromide.....	8,800	25,650
Preparations, medical, alcoholic	.....	46,450
Quinine salts.....	42,300	47,850
Rhubarb.....	8,700	10,300
Santonin.....	31,750	76,450
Senega root.....	42,450	29,250
Sodium borate.....	38,500	70,600
Sodium bicarbonate.....	134,100	135,450
Soda, caustic, raw.....	630,450	584,200
Soda ash.....	564,550	694,250
Chemicals, aromatic.....	.....	14,950
Other chemicals.....	1,689,000	1,633,900
Drugs, etc.....	131,250	66,800

## THE PAPER INDUSTRY IN INDIA

The chief difficulty the paper industry in India has to overcome is lack of raw material, since no wood pulp is to be had in the country. This lack is supplied partly by importation, partly by the use of native grasses, and largely by the use of cotton rags, the supply of which may be judged from the fact that in India over 400,000 tons of cotton goods are used annually. Other raw materials are jute and hemp, and experiments are now being made with bamboo and bagasse, so far without practical results. The *Chemiker-Zeitung*, 38 (1914), 109, gives the following figures for the year 1911: India imported 13,500 tons of raw paper materials worth \$530,000, of which 5,500 tons came from Sweden, 5,000 from England and 1,600 from Germany. The paper consumption amounts to 70,000 tons annually with a value of over \$6,000,000; of this \$2,500,000 worth is of domestic manufacture and \$3,500,000 worth or more is imported. In 1911 there were seven paper factories in operation with a combined capital of about \$2,000,000.

## SCIENTIFIC SOCIETIES

AMERICAN CHEMICAL SOCIETY  
FORTY-NINTH MEETING, CINCINNATI, APRIL 6-10, 1914  
PROGRAM OF PAPERS

## GENERAL MEETING

Addresses of Welcome. HON. F. S. SPIEGEL, Mayor of Cincinnati, and PRESIDENT CHARLES W. DABNEY, University of Cincinnati.

Response. THEODORE W. RICHARDS, President of the American Chemical Society.

The Chemical Problems of an Active Volcano. (Illustrated.) ARTHUR L. DAY.

The Chemical Fitness of the World for Life. L. J. HENDERSON.  
Flame Reactions. W. D. BANCROFT  
Chemical Reactions at Low Pressures. IRVING LANGMUIR

## AGRICULTURAL AND FOOD CHEMISTRY DIVISION

FLOYD W. ROBINSON, Chairman GLEN F. MASON, Secretary

1. Address. FLOYD W. ROBINSON, Chairman
2. Standards of Food and Drug Chemists. EDWARD GUDEMAN.
3. The Determination of Mixed Carbohydrates in Infant Foods. T. M. RECTOR and E. B. WETTENGEL.
4. The Determination of Tannin in Tea. H. C. FULLER.
5. A Rapid Method for the Determination of Sodium Chloride in Butter and its Substitutes. T. M. RECTOR.
6. A Rapid Method for the Determination of Unsaponifiable Matter in Fats and Oils. T. M. RECTOR.
7. The Determination of Caffein in Coffee and Tea. H. C. FULLER.

8. The Official Method for Determining Crude-Fiber as Applied to Cottonseed Meal. CHAS. K. FRANCIS.

9. The Arsenates of Lead. H. V. TARTAR AND R. H. ROBINSON.

10. The Changes Produced by the Wrapping of Bread. H. E. BISHOP.

11. The Determination of Lecithin-Phosphorus in Macaroni and Farinaceous Articles. H. C. FULLER.

12. On the Composition of Lobster. H. S. BAILEY.

13. Tomato Seed Oil. H. S. BAILEY.

14. The Digestibility of Corn Consumed by Swine. S. C. GUERNSEY.

15. Chemical Changes Occurring during the Period of Silage Formation. RAY E. NEIDIG.

16. Preliminary Notes on the Curing of Cucumber Pickles. H. N. RILEY.

17. A Graphic Method of Calculating Diets and Rations. D. L. RANDALL.

18. The Hydrolysis, under Pressure, of Sugar Solutions. W. S. HUBBARD AND W. L. MITCHELL.

19. Notes on the Determination of Total Sulfur. PHILIP L. BLUMENTHAL.

20. Barium in Various Plants. NICHOLAS KNIGHT.

21. The Non-Uniformity of Drying Oven Temperatures. LORIN H. BAILEY.

22. The Analysis of Alkali Soils. C. N. CATLIN.

23. Dates: Comparative Cost of, in Akron, Ohio. CHAS. P. FOX.

24. The Composition of Gooseberries with Special Reference to Their Pectin Content. E. H. S. BAILEY

25. A Rapid Method for Commercial Analysis for Marls and Limestones. O. B. WINTER
26. A Method for the Estimation of Calcium, Strontium, and Magnesium in the Presence of Phosphoric Acid and Iron. O. B. WINTER
27. The Chemistry of the Decomposition of Peat and Muck. C. S. ROBINSON
28. Some Pot Experiments with Mixtures with Peat and Manure in Connection with Various Fertilizers. C. S. ROBINSON

## BIOLOGICAL CHEMISTRY DIVISION

CARL L. ALSBERG, *Chairman* I. K. PHELPS, *Secretary*

1. Coagulation of Albumen by Electrolytes. WILDER D. BANCROFT
2. Colloidal Swelling and Hydrogen Ion Concentration. L. J. HENDERSON, W. W. PALMER and I. H. NEWBURGH
3. The Functions of Ammonia and Phosphoric Acid in the Regulatory Excretion of Acid. L. J. HENDERSON and W. W. PALMER
4. Partition of the Nitrogen of Plant, Yeast and Meat Extracts. F. C. COOK
5. Comparison of the Various Methods for the Quantitative Determination of Sugar in Blood. MAX KAHN
6. Clinical Studies of the Russo Test. MAX KAHN
7. Urinary Catalase in Health and Disease. MAX KAHN and C. J. BRIM
8. On the Presence of Oleic Acid in Gastric Contents of Patients Suffering with Gastric Carcinoma. MAX KAHN and J. SUBKIS
9. The Lipids of Diseased Human Livers. J. ROSENBLUM
10. The Potassium Content of Cerebrospinal Fluid in Various Diseases. J. ROSENBLUM and V. L. ANDREWS
11. The Nitrogen Distribution in Feces. A. R. ROSE
12. A Standard in the Determination of Ammonia by Nesslerizing with the Duboscq Colorimeter. A. R. ROSE and KATHERINE R. COLEMAN
13. Nephelometry in the Study of Nucleases. P. A. KOBER
14. A Soluble Polysaccharide in Lower Fungi. A. W. DOK
15. The Chemical Dynamics of Living Protoplasm. W. J. V. OSTERHOUT
16. The Physiological Water Requirement and the Growth of Plants in Glycolcol Solutions. ALFRED DACHNOWSKI and A. GORMLEY
17. The Estimation of Amino Acids as Such in the Soil. R. S. POTTER and R. S. SNYDER
18. Methods Adapted for the Determination of Decomposition in Eggs and in Other Protein Food Products. H. W. HOUGHTON and F. C. WEBER
19. Factors Influencing the Quality of American Sardines. F. C. WEBER and H. W. HOUGHTON
20. The Composition and Nutritive Value of the Proprietary Infant Foods. F. C. COOK and F. C. WEBER
21. The Electrical Stimulation of Tissue. OLIVER E. CLOSSON
22. A New Apparatus for Determining Crude Fiber in Foods, Feeding-stuffs, and Feces. (Demonstration) A. D. EMMETT
23. The Carbon Dioxide Excretion as Modified by Body Weight. G. O. HIGLEY
24. Enzymes of the Central Nervous System. H. M. ENGLISH and C. G. MACARTHUR
25. Proteins of the Central Nervous System. H. H. MCGREGOR and C. G. MACARTHUR
26. Specificity in the Action of Drugs on Brain and Heart Phosphatids. C. G. MACARTHUR and G. H. CALDWELL
27. Reduction Processes in Plant and Soil. M. X. SULLIVAN
28. The Passage of Nucleic Acid from Plant to Medium. M. X. SULLIVAN
29. Chemical Studies upon the Genus *Zygadenus*. C. L. ALSBERG

## FERTILIZER CHEMISTRY DIVISION

J. E. BRECKENRIDGE, *Chairman* F. B. CARPENTER, *Secretary*

1. Chairman's Address. Chemistry an Important Factor in the Fertilizer Industry. J. E. BRECKENRIDGE
2. The Preparation of Neutral Ammonium Citrate. ERMON D. EASTMAN and JOEL H. HILDEBRAND
3. A Comparison of Neutral Ammonium Citrate with Sodium Citrate and N/10 Citric Acid. PAUL RUDNICK, W. B. DERBY and W. L. LATSHAW
4. The Separation of Organic Nitrogen from Mixed Fertilizers. C. H. JONES
5. Separation of Phosphoric Acid from Lime. F. K. CAMERON
6. Separation of Potash from Kelp. (Lantern.) F. K. CAMERON

## Committee Reports

- Nitrogen. Progress on the Analysis of Commercial Nitrate of Soda. PAUL RUDNICK, *Chairman*
- Phosphoric Acid. G. FARNHAM, *Chairman*
- Potash. J. E. BRECKENRIDGE, *Chairman*
- Phosphate Rock. F. B. CARPENTER, *Chairman*
- Fertilizer Legislation. F. B. CARPENTER, *Chairman*

## INDIA RUBBER CHEMISTRY SECTION

D. A. CUTLER, *Chairman* DORRIS WHIPPLE, *Secretary*

1. The Influence of Temperature in the Physical Testing of Rubber Goods. T. I. WORMLEY and J. B. TUTTLE
2. Review of Report of Joint Rubber Insulating Committee. DORRIS WHIPPLE

The main time of the meeting was taken up with a report of the Analytical Committee and a general discussion

## INDUSTRIAL CHEMISTS AND CHEMICAL ENGINEERS DIVISION

GEO. F. ADAMSON, *Chairman* S. H. SALISBURY, JR., *Secretary*

1. New Volumetric Determination of Sulfur in Iron Ores. L. SELINE
2. Pitot Tubes for the Measurement of Gas Velocities. ANDREW M. FAIRLIE
3. A Comparison of Various Modifications of the Kjeldahl and Dumas Methods for the Determination of Nitrogen in Coal and Lignite. A. C. FIELDNER and C. A. TAYLOR
4. The Mechanism of the Reaction between Phenolic Bodies and Active Methylenes. L. V. REDMAN, A. J. WEITH and F. P. BROCK
5. Fluorescence of Petroleum Distillates. (Lantern.) B. T. BROOKS and R. F. BACON
6. The Manufacture of Gasoline from Heavy Petroleum Oils. (Lantern.) B. T. BROOKS, R. F. BACON and C. W. CLARK
7. Some Economic Phases of the Gasoline Supply. BENJAMIN T. BROOKS
8. Absorption of Caustic Soda by Cellulose. W. D. BANCROFT
9. The Stability of Rosin at Slightly Elevated Temperatures. A. CORRECTION. CHAS. H. HERTY and H. L. COX
10. The Chemists' Club. (Lantern.) WILLIAM L. DUDLEY
11. The Chemist, a Growing Factor in Merchandizing. A. V. H. MORVY
12. The Method of Analysis of Gasoline. G. W. GRAY
13. The Method of Testing Illuminating Oils. G. W. GRAY
14. Coal Ash in Some Unusual Phases. S. W. PARR
15. A Thermoelectric Method of Determining the Purity of Platinum Ware. C. K. BURGESS and P. D. SALE
16. A Nevada Oil Shale. CHAS. BASKERVILLE
17. The Metallography of Malleable Iron. J. CULVER HARTZELL
18. The Pyrometer in the Assay Muffle. F. P. DEWEY
19. Note on a Cause of Spontaneous Combustion in Coal Mines. HORACE G. PORTER
20. Graphical Studies of the Ultimate Analyses of Coals. OLIVER C. RALSTON
21. A Graphic Method of Classification of Coals. OLIVER C. RALSTON
22. Osage Orange: Its Value as a Commercial Dyestuff. F. W. KRESSMANN
23. Some Preliminary Experiments on the Hydrolysis of White Spruce with Sugar and Ethyl Alcohol Yields. (Lantern.) F. W. KRESSMANN
24. A Method for the Rapid Quantitative Analysis of Brass and Bronze. (Pb, Cu, Sn, Sb, Fe, Zn.) R. E. LEE, J. P. TRICKEY and W. H. FEGLY
25. A Method for the Rapid Quantitative Analysis of Babbitt Metals. (Pb, Cu, Sn, Sb.) R. E. LEE, J. P. TRICKEY and W. H. FEGLY
26. The Composition and Testing of Printing Inks. J. B. TUTTLE and W. H. SMITH
27. The Determination of Carbon in Iron and Steel by the Barium-Carbonate Titration Method. J. R. CAIN
28. Determination of Ammonia in Illuminating Gas. J. D. EDWARDS
29. The Iodine Number of Linseed and Petroleum Oils. W. H. SMITH and J. B. TUTTLE
30. Chemical Jurisprudence. LOUIS HOGREFE
31. Report of the Committee on Alum Specifications. WM. M. BOOTH
32. Report of the Committee on Platinum. W. F. HILLEBRAND

## ORGANIC CHEMISTRY DIVISION

F. B. ALLAN, *Chairman* C. G. DERICK, *Vice-Chairman and Secretary*

1. The Chemistry of Enzymic Action. (One hour.) J. U. NEP
2. The Constitution of Acetylacetone-Thiourea. W. J. HALE
3. A Contribution to the Study of the Constitution of Hydroxy-azo Compounds. WILLIAM McPHERSON and GEORGE W. STRATTON
4. A General Method for the Preparation of Orthoquinones. CECIL BOORD and WILLIAM McPHERSON
5. The Oxidation of Propylene Glycol. WM. LLOYD EVANS
6. A Study of the Mechanism of the Grignard Reaction. L. THORP and O. KAMM
7. The Structure of the Three Dihydro- $\beta$ -naphthoic Acids. C. G. DERICK and O. KAMM



8. The Rearrangement of Triarylmethyl Azids. J. K. SENIOR.
9. The Action of Trioxo-methylene on the Aromatic Hydrocarbons in the Presence of Aluminium Chloride. GEO. B. FRANKFORTER AND V. R. KOKATNUR
10. Studies on Organic Periodides. I. Periodides of Methaceticin, Phenacetin and Triphenin. W. O. EMERY
11. Periodides of Antipyrin. W. O. EMERY AND S. PALKIN
12. Molecular Rearrangements of Hydrazines. J. STEIGLITZ AND J. K. SENIOR.
13. The Phosphates of Destearin. R. R. RENSHAW AND R. R. STEVENS.
14. Electromers and Stereoemers with Positive and Negative Hydroxyl. L. W. JONES AND L. F. WERNER.
15. Halogen Substituted Hydroxamic Acids. L. W. JONES AND L. F. WERNER.
16. Formyl- $\beta$ -benzylhydroxylamine. L. W. JONES AND M. C. SNEED.
17. The Addition Compounds of Dimethylpyrone with Organic Acids. JAMES KENDALL
18. Errors in the Dumas Method for Determining Nitrogen Due to Occluded Gases in Copper Oxide. C. A. TAYLOR AND A. C. FIELDNER.
19. The Isomeric Octacetates of Lactose. C. S. HUDSON AND J. M. JOHNSON.
20. Substitution in the Benzene Nucleus and in the Side Chain from the Standpoint of the Electronic Conception of Positive and Negative Valences. H. S. FRY
21. The Salts of Acridine. L. H. CONE.
22. The Action of Halogen on 4-Nitro-*m*-Cresol. L. C. RAIFORD.
23. A Simple Method for the Determination of the Accuracy of the Conductance Data of Organic Electrolytes. C. G. DERICK.
24. The Ionization Constant of Pyracemic Acid. C. G. DERICK AND ST. ELMO BRADY.
25. Symposium - The Teaching of Organic Chemistry.
- I. Theory of Elementary Organic Chemistry. The Teaching of Elementary Organic Chemistry without the Use of Atomic and Molecular Hypotheses. J. B. ALLAN. Discussion.
- II. Theory of Organic Chemistry for Graduate Students. M. T. BOBERT. Discussion. What Shall Be the Character of the Advanced Instruction in Organic Chemistry? R. R. RENSHAW. General discussion.
- III. Laboratory Teaching of Organic Chemistry. The Teaching of Organic Chemistry in the Laboratory. L. W. JONES. Discussion.

#### PHARMACEUTICAL CHEMISTRY DIVISION

F. R. ELDRED, *Chairman*A. P. SY, *Secretary*

1. Methods of Analysis of the Forthcoming Pharmacopoeia. H. W. WILEY.
2. Seasonal Variations in the Iodine Content of the Thyroid Gland. A. HERTON SEIDELL AND FREDERICK FENGER
3. Some Peculiarities of Present Food and Drug Laws. FRANK O. TAYLOR
4. Notes on the Determination of Antipyrine. GEORGE D. BEAL AND DUANE T. ENGLISH.
5. Further Notes on Lloyd's Reagent for Alkaloids. S. WALDBOTT.
6. Estimation of Phenacetin and Acetanilide in Admixture. W. O. EMERY
7. Estimation of Antipyrin. W. O. EMERY AND S. PALKIN.
8. Estimation of Caffeine and Antipyrin in Admixture. W. O. EMERY AND S. PALKIN
9. Estimation of Phenacetin and Salol in Admixture. W. O. EMERY, C. C. LEFEBVRE AND G. C. SPENCER.
10. A Method for the Estimation of Podophyllum Resin. W. M. JENKINS.
11. Commercial Papain and Its Testing. H. M. ADAMS
12. Some Observations on the Leach Test for Coumarin. WILLIAM G. GAESSLER
13. Digitalis Ash. CHARLES T. P. FENNEL.
14. The Estimation of Morphine. H. M. GORDIN
15. The Estimation and Variability of Alcohol in Galenicals. L. F. KEBLER.
16. Results of the Examination of Some Medical Agents in the District of Columbia. L. F. KEBLER
17. Extraction of Morphine from Aqueous Solution. H. BUCH BINDER.

#### PHYSICAL AND INORGANIC CHEMISTRY DIVISION

G. A. HULETT, *Chairman*R. C. WELLS, *Secretary*

1. Rapid Determination of Arsenic in Poison Cases with the Marsh Test. JAMES R. WITHROW
2. The Decomposition Voltages of Salts in Liquid Ammonia. I. The Ammonium Salts. H. P. CADY AND C. A. NASH
3. Adsorption and Stabilization. J. C. BLUCHER AND E. F. FARNAU.

4. The Ideal Diffusion Coefficient and a New Fundamental Law of Diffusion. G. MCP. SMITH.
5. Further Observations on the Preparation of Selenic Acid and Selenates. PHILIP L. BLUMENTHAL.
6. Concerning the Atomic Weights of Carbon and Sulfur. T. W. RICHARDS AND C. R. HOOVER.
7. The Critical Point and the Significance of "b" in the Equation of Van der Waals. THEODORE W. RICHARDS
8. The Present Status of the Absolute Scale of Pressure. THEODORE W. RICHARDS.
9. A Method for Producing a Reproducible Contact Potential between Liquids. E. P. SCHOCH.
10. The Relation between the Concentrations and the Potential of the Ferrous-Ferric Salt Pole. (Lantern.) E. P. SCHOCH.
11. New Electroanalytical Methods for Lead, Tin, Copper and Antimony. (Lantern.) E. P. SCHOCH AND D. J. BROWN.
12. Contribution to the Knowledge of the Actinium Series. HERBERT N. MCCOY AND EDWIN D. LEMAN.
13. Solutions of Some Formates and of Hydrogen Chloride in (Anhydrous) Formic Acid. Cases of Agreement of Strong Electrolytes with the Equilibrium Laws. H. I. SCHLESINGER AND A. W. MARTIN
14. Vapor Pressures in Alcoholic Solutions. O. F. TOWER.
15. Arsenious Oxide as a Starting Material in Acidimetry. ALAN W. C. MENZIES AND F. N. MCCARTHY
16. Equilibria in the Systems: Water, Acetone and Inorganic Salts. GEO. B. FRANKFORTER AND LILLIAN COHEN
17. The Colorimetric Determination of Manganese by Means of Periodate. H. H. WILLARD AND L. H. GREATHOUSE.
18. Electromotive Behavior of Soluble Sulfides. R. C. WELLS.
19. The Phase-Rule Investigation of Addition Reactions. (Lantern.) JAMES KENDALL.
20. Peculiar Action of Iodine. CHARLES T. P. FENNEL.
21. Distribution of Caffeine and Antipyrin between Chloroform and Aqueous Solutions. W. O. EMERY AND C. D. WRIGHT.
22. Reaction in Non-Aqueous Solvents. O. L. BARNEBEY.
23. Separation of Potassium from Sodium by Extraction of their Chlorplatinate with Acetone. O. L. BARNEBEY
24. The Action of Potassium Amide on the Amides of Silver, Barium, Strontium, Calcium, Lithium and Sodium. EDWARD C. FRANKLIN
25. The Action of Potassium Amide on Cadmium, Nickel, and Chromium Salts in Liquid Ammonia Solution. EDWARD C. FRANKLIN.
26. Gas Analysis by Liquefactions and Fractionations. (Lantern.) G. A. BURRELL AND F. M. SEIBERT
27. The Condition of Natural Gas in the Earth's Strata. (Lantern.) G. A. BURRELL AND F. M. SEIBERT
28. Collisional and Diffusional Viscosities. EUGENE C. BINGHAM.
29. The Chemical and Heat Energy of Molecules, Atoms, Sub-Atoms, and Electronic Energy. F. P. SEIBEL.
30. Electrostenolysis. HARRY N. HOLMES.
31. A Burette Calibrating Pipette. C. W. FAULK.
32. Preparation of a Standard Magnesium Salt Solution. C. W. FAULK AND O. R. SWENEY.

#### WATER, SEWAGE AND SANITATION SECTION

EDWARD BARTOW, *Chairman*H. P. CORSON, *Secretary*

1. Sanitary Survey of White River. (Illustrated.) JOHN C. DIGGS.
2. Hypothetical Combinations in Reporting Water Analyses. R. B. DOLE
3. New Apparatus for the Determination of Hydrogen Sulfide in Water. GEORGE B. FRANKFORTER
4. Sanitary Survey of the Ohio River by the U. S. Public Health Service. W. H. FROST AND H. W. STREETER.
5. The Use of Liquid Chlorine in Treating the Water Supply of Indiana Harbor, Ind. H. E. JORDAN
6. Adaptation to Water Analysis of Potassium as Perchlorate. CLARENCE SCHOLL
7. The Preparation of Standards for the Determination of Turbidity of Water. FRANCIS D. WEST
8. Report of the Committee on Standard Methods of Water and Sewage Analysis.
9. Chemical Studies of the Pollution of the Ohio River. EARL B. PHELPS
10. Investigation Relating to the Use of Calcium Hypochlorite as a Disinfectant for Water Supplies. W. G. TICE AND C. H. BLANCHARD
11. Some Further Results of the Hypochlorite Disinfection of the Baltimore City Water Supply: A Comparison of the Reduction of the Different Members of the *B. coli* Group. J. BOSLEY THOMAS AND E. A. SANDMAN
12. Filtration and Softening of the Cleveland Water Supply. HIPPOLYTE GRUENER.
13. The Relation between Aluminium Sulfate and Color in Mechanical Filtration. FRANK E. HALE.

## EXCURSIONS

The Cincinnati Filtration Plant is the largest Mechanical or Rapid Sand Filter Plant in the world. It is a part of the New Water Works which comprise an Intake Pier, Tunnel under River, River Pumping Station, two large Settling Reservoirs, Filtration Plant, three Coagulation Basins, Clear Water Reservoir, 4 1/2 mile Tunnel to Main Station, Main Distribution Pumping Station, several Sub-Pumping stations and many miles of large distribution pipes. The total cost was over 10 million dollars including properties, rights of way, etc.

The purification system, including two settling reservoirs of about 400 million gallons capacity, three coagulation basins of about 22 million gallons capacity, filtration plant and clear water reservoir, cost about 2 1/2 million dollars.

The filtration plant consists of a chemical house, head house and filter house. There are 28 filter units with a total capacity of 112 million gallons per day. All valves, over 200 in number, are electrically operated.

The bacteriological and chemical laboratories are used for controlling the operation of the plant. The laboratory force consists of a chief chemist and bacteriologist, one assistant and a helper.

Since the operation of this plant the city has had an uninterrupted supply of pure, clear and sweet water, and typhoid fever has been reduced over 80 per cent.

Over 150 members and guests of the Society visited this plant; this was a large number considering the fact that there was a steady downpour of rain during the entire afternoon.

The Globe Soap Company Plant at St. Bernard consists of seven buildings connected by 2 miles of private railroad track in an area of 23 acres. The entire factory is steam-heated and electrically equipped. About 75,000,000 lbs. of soap products are produced annually requiring approximately 100,000,000 lbs. of raw materials; 100 cars per day can be unloaded and loaded; about 275 persons are employed and the company maintains a Local Secretary who works directly under the Local Y. M. C. A. carrying on welfare and community work.

Five Chemical Engineers are employed and the entire manufacturing process from start to finish is under strict chemical control.

The Proctor and Gamble Plant at Ivorydale occupies 58 permanent and 22 somewhat temporary buildings in 85 acres of ground. Including the soap, glycerine, stearic acid, red oil, refined oils, lard compound and Crisco, the business of last year exceeded \$50,000,000.

The power plant is fitted for the most part with Sterling boilers, with automatic stokers, and has a rated capacity of 15,000 H. P. All grades of soap are made as well as of glycerine, including C. P. and that for dynamite manufacture. The soap department equipment includes 64 kettles of 150 tons capacity each.

One main laboratory and several small special laboratories examine all raw materials upon arrival and control products and process. The chemical force includes about twelve chemists in the control and research laboratory, besides a number of chemists who have charge of various departments.

The factory employs a force of 1500. A committee looks after all dangerous places and makes recommendations for alterations or safeguarding employees. For over 25 years a Profit Sharing plan that has proven highly satisfactory to both the company and its employees, has been in operation. There are special provisions for medical attendance and all employees are insured in one of the large Insurance Companies, for which the employee pays a small amount and the company the balance.

A very large delegation visited the Globe Soap Works and the Proctor and Gamble Plant on the afternoon of April 8th leaving the University of Cincinnati in special cars. Dainty souvenirs of products were presented to the visitors and a very refreshing tea was served in the Proctor & Gamble Plant.

The National Cash Register Company Plant at Dayton, covers eight city blocks, has thirty-eight acres of floor space and employed 7600 persons in 1913. The annual payroll is over \$6,000,000. The number of registers made in 1912 was 136,489.

## RAW MATERIALS USED IN 1912

11,000,000 lbs. sheet steel	183,994 lbs. tin
5,500,000 lbs. foundry metal	135,602 pieces register slabs
6,500,000 lbs. gray iron castings	602,190 locks
6,800,000 ft. of lumber	610,000 yds. textile
5,000,000 lbs. of paper	236,893 pieces glass
3,129,006 lbs. copper	38,392 tons coal

Of the fifteen men on the laboratory staff, there are four chemists, two chemical engineers, two mechanical engineers and two mechanically trained men. Chemical control is accomplished by means of process specifications covering many shop operations such as staining, enameling, varnishing, mixing of alloys, fluxes, etc.

The laboratory controls the operation of the water softener, purity of the water supply, food and milk supply, purchase of materials (80 specifications), fuel and lubrication. As an unusual duty of the laboratory, many talks on simplified physiology and health subjects have been prepared.

The welfare and educational work of this company among its employees is well known to the industrial world.

## NATIONAL CASH REGISTER COMPANY ITINERARY

Arrived in Dayton, 9.15 A.M.  
 Assembled for photograph.  
 Factory lecture in Hall of Industrial Education. (Illustrated by slides and kinemacolor motion pictures) 9.40 A.M.  
 Trip through factory (Party divided into groups and furnished with guides), 10.30 A.M.  
 Luncheon in Officers' Club, 11.45 A.M.  
 Train for Middletown, 12.45 P.M.

The American Rolling Mills at Middletown, in 1832, made the first crucible steel produced in the U. S. This mill is the home of Ingot Iron. The plant known as the East Works, finished in 1911, is the most up-to-date of its kind in the country.

## AMERICAN ROLLING MILLS COMPANY ITINERARY

Address of Welcome, George M. Verity, Pres.  
 Inspection of East Works, 2.15-3.30 P.M. (Parties divided into groups of twenty-five each; each group in charge of a competent guide).  
 Route during inspection of East Works: Open Hearth Department; Boiler and Power House; Soaking Pit, Blooming Mill, and Bar Mill; Sheet Mill; Annealing Department; Galvanizing Department; Shipping Department.  
 Entire party transferred by train to Central Works for inspection of Research Laboratory.  
 Inspection of Research Laboratory, 3.45 to 4.30 P.M.  
 Refreshments served in Warehouse.  
 Train left for Cincinnati, 5.00 P.M.

In his address, Mr. Verity stated that his company are spending large sums on chemical control and research, with the result that many fallacies in methods of procedure have been corrected and their products greatly improved.

The New Cincinnati City Hospital occupies grounds covering 27 acres. The power house is a 2000 H. P. plant, equipped with three dynamos and an ice-making machine, and having four of its boilers equipped for burning natural gas.

The Lloyd Library and Museum contains forty thousand volumes devoted to Botany, Pharmacy, Materia Medica and allied sciences with a section of eclectic medicine. The institution is incorporated, is free to the public, will never be sold, and will always remain a public institution for the benefit of science.

The National Lead Company Plant at Cincinnati is in five acres of grounds, has 75,000 sq. ft. of floor space in its buildings and 60,000 sq. ft. in its corroding yard; 10,000 tons of raw materials are used annually. The employees number 175 and the annual payroll is \$175,000. No effort is spared to insure the best working conditions for the employees; locker rooms shower baths, dining and rest rooms and a kitchen are furnished and personal cleanliness required. One chemical engineer supervises the chemical control which is exercised throughout the process.

The Lunkenheimer Company, occupying over 500,000 sq. ft. of floor space, has the largest plant in the world devoted exclusively to the manufacture of high-grade engineering specialties. These include almost numberless articles used in steam and

marine engineering, in motor engines, in automobiles, and allied branches. Much of the company's reputation is based on its valves and fittings for extra high pressure and superheated steam. There are two foundries, one being for the non-ferrous metals and the other for the ferrous metals such as cast-iron, semi-steel, malleable cast-iron and special iron alloys. All departments are under chemical control, for which purpose the plant is excellently equipped with analytical, research and physical laboratories. These laboratories link together the sciences of metallurgy and steam engineering. The fullest provisions are made for preserving the safety and welfare of the employees, and a perfectly furnished hospital is centrally located in the plant and under expert supervision.

**W. T. Wagner's Sons** prepare artificial Mineral and Table Waters from pure distilled water and is one of the two firms in the U. S. that follows the chemical analyses of natural waters as a standard for artificial waters. The factory covers 16,000 sq. ft. of ground with 50,000 sq. ft. of floor space. The factory equipment includes two 100 H. P. Tubular Boilers and a water still having a daily capacity of 2500-3000 gals. All pipe lines and tanks for cold water are of Block Tin and those for steam and hot water lines are tinned copper. Over 600,000 gallons of finished products are made annually. The chief chemist who is a recognized authority on mineral water manufacture is in charge of a very complete research laboratory for bacteriological and chemical investigation, the equipment of which includes a fine Leitz Microscope and Kruss Spectroscope. Proper safety and welfare provisions are provided.

**The Eagle White Lead Company** uses about 2 million lbs. of raw materials annually and turns out 2 1/2 million lbs. of finished products. About 250 men are employed on a \$200,000 payroll. The plant is under chemical control. The Old Dutch Process of Corrosion is used. In addition to white lead in dry form and ground in oil, other lead pigments are produced as well as Plumbers' Metal Supplies such as lead pipe, traps, bends and solders of Babbitt metals. The welfare work is chiefly done in connection with the habits of cleanliness necessary for good health and safety.

**The Wm. S. Merrill Chemical Company** manufactures pharmaceutical products and is one of the three oldest concerns in the city. The founder of the business was said to be the first chemist in the Ohio Valley.

**The "Icy-Hot" Bottle Company**, only five years old, now manufactures 400 models of bottles, jars, carafes, pitchers, luncheon outfits, etc., each embracing the original vacuum principle.

**The Fleischmann Company** are manufacturers of compressed yeast in the U. S., Canada, Mexico and Cuba. The last ten years have brought about great changes in the methods and processes of manufacture and while originally compressed yeast was a by-product of the distillery it is today the main product of the Fleischmann factories; distilled spirits and distilled vinegar are the by-products of their various plants.

**The Frank Tea & Spice Company** attribute their success and reputation for pure products to the closest chemical supervision of the products of importation. The firm is one of the largest importers, grinders and manufacturers in this line.

**The Dolly Varden Chocolate Company and Colgate & Company** expressed their appreciation of what chemical science has done for them by presenting the lady members and guests with souvenirs of their productions.

**The Cincinnati Health Department Laboratory** exercises the most rigid control of all food products as well as offering free medical attention to all its school children in connection with free clinics.

**The National Biscuit Company—Muth's Bakery**—makes bread only—over 100,000 loaves daily.

**The U. S. Food and Drug Inspection Laboratory** is a branch of the Bureau of Chemistry, Department of Agriculture. Its purpose is to carry out the provisions of the Food and Drug Act of June 30, 1906.

**The Union Distilling Company Plant** was entirely wiped out by fire in 1909 but was rebuilt in 1910 and is now a model as to construction and equipment.

The following plants and institutions were also open to visitors:

<b>Andrews Steel Co.</b>	<b>The Zoological Garden.</b>
<b>Wiedemann Brewing Co.</b>	<b>American Oak and Leather Co.</b>
<b>Old "76" Distilling Co.</b>	<b>J. H. Day Co. (Special Machinery).</b>
<b>James Heekin Spice Co.</b>	<b>Laidlaw-Dunn-Gordon Co. (Pumping Machinery).</b>
<b>American Diamalt Co.</b>	<b>U. S. Public Health Service Laboratory.</b>

## INDUSTRIAL CHEMISTS AND CHEMICAL ENGINEERS DIVISION—REPORT OF COMMITTEE ON ALUM SPECIFICATIONS

[It was voted by the Division that this report be printed in THIS JOURNAL, so as to give time for study and discussion of the specifications included, preparatory to final action at the Montreal meeting.—EDITOR.]

**COMMERCIAL ALUM**—Shall contain not less than 16 per cent alumina ( $Al_2O_3$ ) and not more than 1.25 per cent iron ( $Fe_2O_3$ ).

Shall be free from foreign matter, mechanically mixed through mass.

**STANDARD GRADE**—Shall be a clean product, containing not less than 17 per cent alumina ( $Al_2O_3$ ), nor more than 50 per cent iron, figured as  $Fe_2O_3$ . Shall be slightly basic.

**NEWSPAPER ALUM**—1. Must be readily soluble in water.

2. Practically free from insoluble matter other than alumina. (Insoluble alumina in small amount will not be considered objectionable.)

3. It shall contain not more than 1.00 per cent total iron, calculated as ferric oxide ( $Fe_2O_3$ ), nor more than 0.05 per cent of iron, calculated as ferric oxide and present in the ferric condition.

4. It must contain no free acid.

5. Must contain not less than 17 per cent alumina ( $Al_2O_3$ ) combined in the form of sulfate and soluble in water.

6. (Optional.) It must, unless otherwise specified, be ground to pass a 10 mesh sieve.

**IRON FREE ALUM**—1. It must be readily soluble in water.

2. It must be practically free from insoluble matter other than alumina (insoluble alumina in small amount will not be considered objectionable).

3. Must be snow-white in color.

4. Shall not contain more than 0.05 per cent iron, calculated as  $Fe_2O_3$ .

5. Must contain no free acid.

6. Shall contain not less than 17 per cent alumina ( $Al_2O_3$ ) combined in the form of sulfate and soluble in water.

7. (Optional.) It must, unless otherwise specified, be ground to pass a 10 mesh sieve.

**FILTER ALUM**—1. Must be readily soluble in water.

2. Insoluble matter must not exceed 0.15 per cent.

3.  $Al_2O_3$ , at least 17 per cent.

4. Basicity, at least 3 per cent of the total alumina ( $Al_2O_3$ ) present, *i. e.*, a 17 per cent alum must contain 0.51 per cent basic alumina ( $Al_2O_3$ ).

5. Iron must be less than 0.65 per cent reckoned as  $Fe_2O_3$ .

6. Payment made on actual percentage alumina ( $Al_2O_3$ ) present.

**COLOR MAKERS' ALUM**—1. Must be readily soluble in water.

2. Insoluble matter shall not exceed 0.15 per cent.

3. Must be free from dark and gritty matter.

4.  $Al_2O_3$ , at least 16 per cent.

5. Must be basic.

6. Iron must not exceed 0.01 per cent reckoned as  $Fe_2O_3$ .

**SAMPLING AND WEIGHING**—A separate sample is to be taken



from a number of barrels, in good condition, representing at least 5 per cent of the total shipment, each sample to be taken from the middle of the barrel. The individual samples are to be thoroughly mixed and quartered and reduced down to sufficient size, into two equal portions marked A and B. Each portion is to be immediately enclosed in an air-tight bottle and each bottle marked with initial A or B, with date and car number identifying the shipment.

Portion A is to be considered available for test by purchaser and B is to be considered available for test by seller.

Shipper and consumer are each to sample in this manner at shipping and receiving points, respectively.

In case of disagreement on tests between buyer and seller, all portions of all four samples remaining are to be submitted to independent reference laboratory to be agreed upon, and quality, as determined by said reference laboratory is to be final, and the cost of reference work to be paid by the party most in error.

That portion of a shipment of alum which does not fulfill the requirements upon independent test as herein provided for, as proof thereof may be rejected, the shipper paying the freight both ways on the rejected material; or such shipment may, at the option of the consumer, be accepted and claims made commensurate with the degree of shortage or of inferiority as determined by the herein provided independent investigation.

WM. M. BOOTH.

#### THE AMERICAN ELECTROCHEMICAL SOCIETY TWENTY-FIFTH GENERAL MEETING NEW YORK CITY, APRIL 16-18, 1914

The Twenty-fifth General Meeting of the American Electrochemical Society was held in New York City, April 16-18, 1914, the sessions being in The Chemists' Club and Earl Hall, Columbia University.

Friday, April 17th was given over to an all-day excursion by steamboat around New York Harbor and Staten Island. The plants of The American Smelting and Refining Company, The United Lead Company and The Waclark Wire Company were visited. This excursion and the Smoker at the Chemists' Club on Friday evening were complimentary to the guests, being tendered by the New York Section of the Society. A Subscription Dinner Dance at The Chemists' Club closed the meeting.

#### PROGRAM OF PAPERS

- Some Economic and Aesthetic Aspects of Electrochemistry. Presidential Address. (Printed in full below.) E. F. ROEBER  
Characteristics of Electrical Energy as Affecting Chemical Industries. C. P. STEINMETZ.  
Efficiency of Power Transmission *versus* Utilization in Local Electrochemical Industries. P. SOTHMAN.  
Some Economies in the Use of Energy in Electric Furnaces. F. A. J. FITZGERALD.  
Power for Electric Furnace Work. W. S. HORRY.  
Electrolytic Flames. (Illustrated.) WILDER D. BANCROFT.  
Electric Steel Castings. C. A. HANSEN.  
Electric Furnaces for Steel Making. EUGENE B. CLARK  
Advantage of Southeastern Alaska for Hydroelectrochemical Industries. W. P. LASS  
Progress in Leaching and Electrolytic Treatment of Copper Ores in South America. E. A. SMITH.  
Hydro-electrometallurgy of Copper. ROBERT R. GOODRICH.  
Leaching of Copper Tailings. RUDOLPH CAHL  
Metal Inventory in an Electrolytic Copper Refinery. RALPH W. DEACON.  
Addition Agents in the Deposition of Zinc from a Solution of Zinc Sulfate. O. P. WATTS AND A. C. SHAPE  
The Effect of Addition Substances in Lead Plating Baths. FRANK C. MATHERS AND O. RALPH OVERMAN  
Electrodeposition of Cadmium. FRANK C. MATHERS AND HUGH M. MARBLE.  
Electrodeposition of Nickel. C. W. BENNETT, H. C. KENNY AND R. P. DUGLISS  
Electrolytic Deposition of Brass on a Rotating Cathode. C. W. BENNETT AND A. W. DAVISON.

A New Method for the Determination of Free Cyanide in Electroplating Solutions. GUSTAVE E. F. LUNDELL.

Electric Conduction at High Temperatures and Methods of Measurement. (Illustrated.) E. F. NORTHRUP.

A New Railway Track Cell. E. L. MARSHALL  
Laboratory Notes on Some Electrical Properties of Silver Sulfide. F. A. J. FITZGERALD

Polarization Single Potentials. CLAUDE N. HITCHCOCK  
New Cell Arrangements for Direct Determination of the Free Energy. REINHARD BEUTNER

Experiments on White Lead. R. STUART OWENS.  
A Microscopic Study of Electrolytic Iron. OLIVER W. STOREY

The Effect of Addition Agents in the Electrodeposition of Iron. O. P. WATTS AND M. H. LI

The Permanency of Base-Metal Thermocouples as Affected by their Microstructure. O. I. KOWALKE.

The following papers had already been presented before the New York Section and were discussed:

The Power Problem in the Electrolytic Deposition of Metals. LAWRENCE ADDICKS.

The Power Problem in the Electrolytic Deposition of Metals. H. E. LONGWELL.

Sources of Direct Current for Electrochemical Processes. F. D. NEWBURY.

Improvements in the Metallurgy of Zinc. G. C. STONE.  
Electric Zinc Smelting. W. R. INGALLS.

Electrolytic Zinc. JOS. W. RICHARDS.

#### PRESIDENTIAL ADDRESS

#### SOME ECONOMIC AND AESTHETIC ASPECTS OF ELECTROCHEMISTRY

By E. F. ROEBER

There is beauty in electrochemistry. The late Ludwig Boltzmann once said that of all artists the mathematical physicist is nearest to the World's creator in the simplicity, directness, and economy of his methods; Boltzmann made this remark in appreciation of the work of Kirchhoff and Maxwell. But we can apply it with equal truth to the electronic theory of our own time which in the simplicity of its fundamental conceptions and in the comprehensiveness of its outlook has all the elements of pure beauty. The intellect which builds the structure of the atoms of the different chemical elements out of a positive electric nucleus in association with varying numbers of negative electrons, and makes his atoms produce the desired result, is a true creator and his model has a beauty like that of the visible world around us.

But more beauty is hidden in electrochemistry than the mathematical beauty of electrochemical theory. The research electrochemist who works out a new process, whether it is the production of aluminum from its oxide or the conversion of amorphous carbon into graphite or the production of calcium carbide from lime and coke or whatever else, proceeds exactly along the same methodical lines as the artist, whether he be sculptor or painter or poet. The artist must take nature as it is. But for his work he takes from nature only what his imagination tells him to be essential to the idea he has in mind. It is this selective copying of the essential from nature and this restriction to the essential that makes a work of art beautiful.

The method is exactly the same with the creative electrochemist. He cannot improve on Nature's processes and methods. All he can do is to imitate or copy Nature's processes and combine them to a certain end. But because his goal is a certain product he can select the starting materials which are essential and use nothing else, and he can select those processes of production which are essential and combine them into the most direct way of production and produce only what is wanted. Artificial graphite made in the laboratory is superior to natural graphite, because nature does not set out to make pure graphite and man does. This makes the economic value of artificial graphite, but it also makes the artificial graphite process in the bold directness of its execution a true work of art. Wherever a process is so designed as to reach its object in the most direct

way with greatest economy, it is beautiful in the eyes of those who understand its rationale and this is broadly true and not restricted to electrochemistry. But the trained engineer's or scientist's intellectual eye is needed to see this type of beauty.

The thoughts on some particular aspects of electrochemistry which I want to submit to you for reflection to-night are of a cognate nature. They refer to the part which electrochemistry plays in the change now going on in modern civilization in economic and aesthetic valuations. Our age is called an age of unrest and revolution. Whether we are really so much more restless than our ancestors is open to discussion and hard to decide. But that the scientific and concomitant engineering advances of the last century have brought an entirely new phase (in the phase-rule sense) into the play of human reactions which make up the history of mankind, is not open to question. That the effects of modern science and engineering go far beyond their spheres of immediate interest is undisputed. What then is the effect of electrochemistry on two apparently so remote fields as political economy and aesthetics?

To express the question concisely I borrow Friedrich Nietzsche's phrase of the revaluation of values. My subject is: How does electrochemistry bring about a revaluation of economics and aesthetic values? I have brought Nietzsche's name into this discussion for still another reason. Nietzsche's brilliant and at first sight extraordinarily daring attempt of a revaluation of ethical values for the sake of creating the "Uebermensch" is perhaps in the final analysis of its positive aspects nothing more than a robust reassertion of what was strong and healthy in the viewpoints and valuations of classic Greece and Rome, but has been lost in the last nineteen centuries to an exaggerated weak sentimentality. Nietzsche wanted to make restitution of this lost strength and health from classic Greece to modern civilization and then create a new ethics. Now, it would seem that the effect of science and engineering on aesthetics is acting at present in the same direction in emphasizing the necessity of a return to the aesthetic viewpoint of classic Greece, as embodied in Socrates' view of the kinship of beauty and utility. It is for this reason that before speaking of aesthetic aspects of electrochemistry it is necessary to take up its economic aspects.

How are economic values being created by industrial electrochemistry? For this discussion Prof. Karl Knies' old and well-known conception is very useful that economic value is of three kinds—*place value*, *time value*, and *form value*. If I may use the text book illustration, ice in winter in the Maine woods has no economic value because there is no market for it there. Brought to New York, it gets place value, because there is a demand for it in New York. Stored and sold in summer time, it gets an additional economic value—*time value*. Nothing has been done to the ice itself by man. The place value has been created by transportation, the time value by storing, and as we shall see later these two points are of importance for the production of economic values by electrochemistry.

But for the present let us consider the third kind of economic value—*form value*, *i. e.*, the value created by the work done by man on the materials of nature, comprising mechanical work as well as chemical changes. Any chemical reaction produces or annihilates form values economically speaking. But what is the distinguishing characteristic feature of the form values produced by the electrochemical industries? Let us take a few typical examples.

By the electrolysis of a solution of common salt we get caustic soda and chlorine and we work up the latter perhaps into bleaching powder. The excess of the value of the caustic soda and bleaching powder over that of common salt is the form value produced by this process. So it is in the production of calcium carbide from lime and coke, of nitric acid and nitrates from atmospheric nitrogen and so on.

The fixation of atmospheric nitrogen representing an extreme case is most instructive. The raw material is atmospheric air which as such has no economic value at all, so that we might say that in the production of nitrate from air the economic efficiency becomes infinitely high. It sounds very well to speak of a process with an infinitely high economic efficiency, but if we take the time to remember that exactly this process which is now worked with fair financial results in Norway turned out a commercial failure some ten years ago in Niagara Falls, it is evident that our consideration must have been in some way so one-sided as to be misleading.

Why was fixation of atmospheric nitrogen a failure at Niagara Falls and why is it a success in Norway? Not primarily on account of the process because the Bradley-Lovejoy process worked with about the same technical efficiency as the Birke-land-Eyde process, though the apparatus was considerably more complicated. No, the decisive element which caused failure at Niagara Falls and success in Norway, is the cost of electric power which is three to five times lower in Norway than at Niagara Falls. And this brings us right to the root of the whole matter.

In discussing the economic value of some electrochemical products we have so far in a one-sided way compared only the value of the starting materials and of the end products, but we have entirely neglected the fact that in these cases we have not only to do with materials as such, but rather with the storage of energy in materials. The form value of many products of electrochemical industries is essentially due to their high energy content. A large amount of chemical energy is stored in electrochemical products; it is latent under ordinary condition, but it may be gotten out wherever and whenever necessity arises and this fact makes them useful and economically valuable.

Let us carry this consideration a little further by making use of the conception that the energy of a given system may be considered as the product of two factors—the capacity factor and the intensity factor, to use the terms of Ostwald. The total amount of energy remains the same. But for the engineering applications it makes an enormous difference whether we make the capacity factor small and the intensity factor large or the former large and the latter small.

In case of a waterfall the amount of water passing over the fall in a certain time is the capacity factor, the height of the fall is the intensity factor. The engineering requirements of the development of a waterfall with little water and a high fall are very different from the case of a lot of water with a small fall, though the energy may be exactly the same in both cases.

In the case of electrical energy the current passing in a certain time, measured in coulombs, is the capacity factor, the pressure in volts is the intensity factor. For electric power transmission we make the intensity factor the voltage, as large as possible, in order to decrease the transmission loss.

In the case of electrochemical products, the weight of the materials is the capacity factor, the specific energy stored in them per unit of weight is the intensity factor. If we make the latter high, if we store a lot of energy in a little matter, it will again be favorable as reducing the cost of transportation.

Now the element of transportation brings us to the conception of the place value of electrochemical products. If their form value is due to their high energy content, their place value is due to the possibility of chemical power transmission by material transportation of electrochemical products. These products of the electrochemical industries which are characterized by a high specific energy content are the principal medium of chemical power transmission.

There are two points of chemical power transmission to be specially emphasized. One is that it is not bound to a fixed route. It requires no line wires. It makes use of the ordinary transportation facilities for materials—railways, ships, etc.

This is important as it opens fields for chemical power transmission where electrical power transmission fails. For instance, there are still very large areas in this country, Canada and elsewhere which are so little populated that it would not pay to erect an electric transmission system to provide electric lighting. Here acetylene lighting is of supreme importance. Acetylene lighting is a case of chemical power transmission. At Niagara Falls the electric furnace produces calcium carbide from lime and carbon and chemical energy is thus stored in the carbide which is transported with its energy to any place where acetylene is required for lighting.

If transportation creates place value, storage creates time value. The use of chemical energy after it has been transmitted is not limited to a certain time and that is the second important feature of chemical power transmission. With electrical energy which cannot be stored as such, it is necessary to use the transmitted energy at once or to provide special means for storing it. In this respect chemical power transmission differs essentially from electric power transmission and is superior to it. Chemical energy is in itself essentially stored latent energy and is used, therefore, in connection with other systems of power transmission for storage purposes, as in the case of storage batteries for electric power systems. The time value of calcium carbide is due to the fact that we can store it and can produce the acetylene just at the moment when it is needed for lighting.

There is a long list of electrochemical products which may be considered from the viewpoint of chemical power transmission. In bleaching powder we transmit the possibility of producing a bleaching or a disinfecting liquid whenever and wherever it is needed. In the series of peroxides we transmit their avidity to give off an atom of oxygen when and where we want it, or the reaction caused by it.

As pretty and concrete an illustration of chemical power transmission as we may wish we have in Hans Goldschmidt's ingenious aluminothermic reaction. The heat of reaction of aluminum and oxygen in forming alumina is relatively very high per unit of weight of aluminum. This is just the reason why the economical production of aluminum from alumina did not succeed until electrolysis was resorted to. Now the fundamental idea of the aluminothermic method is that we have in metallic aluminum a medium which gives us by combination with oxygen a large amount of energy wherever or whenever needed. In thermit, the mixture of aluminum and iron oxide, we transport essentially the capability of producing at any place and at any time, highly superheated molten steel for welding rails, for making repairs, and so on.

Again in the new and important Norwegian nitrate industry we have an example of what we may call international chemical power transmission, as the economical value of Norsk saltpeter depends on its easy transportation by ship to other countries. Thus we have at the same time creation of economic values in Norway by building up a new and important industry and creation of economic values in other countries by using Norsk saltpeter to further agriculture.

I have dwelt on the relation of electrochemistry to chemical power transmission at such length because so many electrochemical products can be considered from this viewpoint. But it would be wrong to think that the whole of electrochemistry can thus be viewed. There are quite a number of very important electrochemical products in which with no stretch of imagination I am able to detect time value. But in all cases the form value is high.

In the case of aluminum we have the aspect of chemical power transmission only in the aluminothermic reaction, which though big in itself uses only a small amount of the total output of aluminum. In cooking utensils, in line-wire construction and other applications it is simply the mechanical and electrical

properties of aluminum which count and which give it a high form value.

In electrolytic copper refining, the oldest and certainly one of the biggest electrochemical industries, the increase of form value is remarkable. It is a double one: (1) The gold and silver are recovered; (2) the copper itself is considerably increased in form value, due to its greater purity and resulting higher electric conductivity.

All those products of electrochemical industries which have nothing to do with chemical power transmission have a high form value and must have it because otherwise it would not pay to use an electrochemical process in view of the high cost of electrical power. Hence, the well-known axiom that in all such applications the use of electrochemical processes should be restricted as much as possible to the finishing touches, that is, to the refining of a comparatively advanced product.

In addressing the American Electrochemical Society I need hardly show at length how this creation of economic values by the electrochemical industries has affected and is affecting modern civilization in its various phases. What was waste before, and what was considered a nuisance, becomes valuable. When the early Colorado gold seekers discovered the tungsten ores in Boulder Canyon, they cursed them as they were not what they wanted. But "heavy black sand" electrochemistry has given to civilization ferro-tungsten and the tungsten lamp. From culm, the waste material of the anthracite coal mines, Acheson has given to the world artificial graphite with its numerous applications. Then there are the enormous electric-furnace industries of artificial abrasives in use in so many walks of life. And so I could go on through the list of electrochemical products down to Cottrell's electrostatic process of recovering values from obnoxious smelter fumes. I should add, however, that electrolytic copper refining, itself made possible by the dynamo, has paid its debt to electrical engineering and by furnishing firm high-conductivity copper has made modern electric power transmission possible. And as we have seen, in chemical power transmission electrochemistry has brought into modern civilization an absolutely new element by which what is now waste power is being scattered all over the world to build up industries, to further agriculture with fertilizers, to light cities with acetylene, to aid public health with bleaching powder and to affect civilization in general in its most heterogeneous aspects. That electrochemists as true creators are bringing about a revaluation of economic values there can be no doubt. But what has electrochemistry to do with aesthetics?

If beauty is perceived through our senses, the first question is: How has modern engineering affected our senses? The answer is simply that modern engineering has given us artificial senses in addition to our natural senses. In the old days when the apparatus in physical and chemical laboratories were home-made affairs, it was said that experimental physicists and chemists should be able to see with their ears and hear by touch, smell with their tongues and measure temperatures with their eyes. Now modern engineering has given us instruments and apparatus which really represent new senses and which are available to a much more general public. And what is more, our artificial senses can be repaired or replaced by new and better ones and they give us permanent records.

I am not stretching the meaning of the term senses in speaking of instruments as artificial senses. To the electrical engineer the readings of the voltmeter and wattmeter are as real and as true indications of the outside world as though he put his head out the window to feel whence the wind blows. Pyrometers give as real, though much more exact indications of temperature, as the touch of a hot body by hand or the trained eye of the furnace man. The photographic camera is a new artificial eye that preserves the record of what it sees. Successive photographs put together in a moving picture show enable us to



crowd into a period of five minutes what may have happened in a year. We can see crystals and plants grow. The electric oscillograph gives us a record that permits us to see in leisure transient phenomena that happen in portions of a second, and study over them for hours. The telephone stretches the ability of the human ear so that it can hear in Denver what is said in New York. And if we hear our children of three or four years talk to us over the long-distance telephone in such a self-evident matter-of-fact way as though they were sitting on our knees, we cannot escape the conclusion that a new generation is rising to which the perception of the outside world comes through new senses and which consequently looks at the world with new eyes. What has electrochemistry to offer to this new generation in aesthetic ideals?

It seems to me that the fundamental contribution which electrochemistry has to make to aesthetics is to carry to its last consequence the principle that waste can never be beautiful. Of course this principle is as old as art. Waste of words in a work of literature, waste of lines or colors in pictures, waste of space in architecture have always been considered the opposite of beautiful. But the growing multiplicity of our sensual knowledge due to the magnified and projected extension of our senses forces us to see waste where our ancestors saw beauty and had a right to see beauty.

Permit me to concentrate my remarks on the one subject that is uppermost in this connection in the minds of American electrochemists—the question of the power development of Niagara Falls. I use it as a clear cut example of what revaluation of aesthetic values by electrochemistry means. The magnificent group of electrochemical industries of Niagara Falls which are the pride of every American electrochemist and should be the pride of the whole American nation suffers seriously from the power famine due to the cessation of power development by international agreement between the United States and Canada. This agreement is based on the alleged will of the people of both countries to have the falls preserved as a scenic spectacle on the principle of conservation of natural beauty. The battle cry is conservation of natural beauty for the people.

The counter-argument has been made that the natural beauty conservationists want to conserve something that no longer exists. With this I agree, but I cannot agree with the expression usually given to this argument, that, if Niagara Falls could be preserved in its original magnificence, it would be worth while but that Niagara as a majestic spectacle has never belonged to the present generation and that its beauty has been given up to noisy and offensive exploitation long before the first power station was created.

This may be true, but it seems to me that this argument does not reach the root of the matter. The beauty of Niagara Falls, like all beauty, is subjective in the onlooker. The question is simply: What do we see when we stand at the brink of Niagara Falls?

Our ancestors who knew nothing of the principle of conservation of energy, of transformation of different forms of energy into each other looked simply at the material side of the Falls and saw beauty and had a right to see beauty. And if we force ourselves into such a one-sided attitude of mind, we can still see beauty.

But if we stand as modern men at the Falls with a free attitude of mind, we don't see simply water, we see power. We see the possibilities of using this power for electric power transmission for lighting, traction, and industrial purposes on a wider area. We see the even greater possibility of storing this power in electrochemical products and utilizing them all over the land in all walks of life. If we look at the Falls with this attitude of mind which is the natural one for us, every cubic foot of water that goes thundering over the falls unutilized appeals to us as waste and nothing but waste.

Now waste can never be beautiful. If the artist's selection of the essential and nothing but the essential makes a work of art beautiful, anything that strikes our imagination as waste must prevent aesthetic enjoyment. If we could look at Niagara Falls with the eyes of our ancestors it would be different, but in full possession of our extended senses which an engineering age has given us, the Falls of Niagara—as much of them as is not utilized—must simply impress us as a waste of immense proportions.

And just the element of bigness which was an element of beauty to our ancestors, has necessarily become to us the reverse, emphasizing only more emphatically the criminal negligence of letting waste on such a tremendous scale go on. Undeveloped, Niagara Falls remains spectacular even to the modern man, but it is no longer beautiful.

The perverse mind of Nero could enjoy the spectacle of Rome burning. A savage tribe could naively enjoy a conflagration that would consume for spectacular purposes a million tons of coal a week. We let the equivalent waste go on in water-power and hear it called saving beauty for the people.

But there is little use in arguing in aesthetic matters. All we can really do is to make people see for themselves, use their own senses, all of them, their natural ones and their artificial ones. This is what the engineering developments tend to do every day and we can depend upon it that as surely as day follows night, a new generation is rising that will use its senses, all of them, and make its own aesthetics.

When that time has come, the Falls of Niagara running dry will reveal to the world immense beauty, health and wealth scattered by electrical and chemical means all over the country, while the grandeur of the whirlpool rapids, unchanged and undiminished, will have a higher aesthetic value, a deeper meaning of beauty than they can possibly have for us. The world will then smile at the aesthetic scruples of so many well-meaning people of our own time and will wonder what all that talk of saving Nature's beauty was about.

#### THE AMERICAN INSTITUTE OF ELECTRICAL ENGINEERS—293rd MEETING

The 293rd meeting of the American Institute of Electrical Engineers was held in Pittsburgh, April 9–11, 1914. About 200 members attended.

Wilfred Sykes presided at the first day's session, which was largely devoted to a discussion of the use of electricity in mines. H. O. Swoboda presented a paper on "Self-Contained Portable Electric Lamps," in the course of which he demonstrated an incandescent lamp which may be used in any position and so protected as to resist damage and to prevent the emission of sparks on rough handling.

H. H. Clark discussed "The Regulation of Electrical Installations in Mines." Among other matters dealt with were the rules proposed by the Bureau of Standards, American Mining Congress, and the English and German laws for electrical installations in mines.

The banquet was held on Thursday evening, April 9th. A. M. Dudley, chairman of the Pittsburgh Section of the Institute, delivered the address of welcome.

On April 10th, safe mine operating and the installation of electric signal and telephonic systems were taken up and discussed; and G. M. Eaton read a paper on "The Development of the Electric Mine Locomotive."

On April 11th, the convention closed after trips of inspection to the Westinghouse plants and to the station of the Bureau of Mines.

W. A. HAMOR.

# NOTES AND CORRESPONDENCE

## THE INVENTION OF CELLULOID

*Editor of the Journal of Industrial and Engineering Chemistry:*

Being the author of the article on celluloid in the new edition of Thorpe's "Dictionary of Applied Chemistry," from which Prof. Chandler submits a mangled quotation with his emphatic disapproval,<sup>1</sup> and looking back on thirty years' experience in the celluloid industry, I feel constrained to reply to the remarkable statements of the learned Professor.

At the risk of wearying the reader, I must rehearse that part of the history of the nitrocellulose industry which bears on the pyroxylin-camphor compound best known as celluloid. I concede at the outset that the word "celluloid," the registered trade mark, was coined by one of the Hyatt brothers and that several books on the industry, all of them written by outsiders, and some of them not fit for a kindergarten course, ascribe the invention to Hyatt or the Hyatt brothers. Even Beilstein's great handbook falls into this error. All of this goes to show that a legend skillfully launched and brazenly defended is tenacious of life.

The first mention of camphor in conjunction with pyroxylin is contained in the British Patent 1,638 of July 26, 1854, granted to James A. Cutting of Boston, U. S. A., for photographic pictures. Cutting dissolves 32 grains of camphor in a pint of collodion, already containing 80 grains of potassium iodide, and claims by this addition to increase the vigor and distinctiveness of delineation of the positive picture and particularly the half tints, also the beauty of the picture, by giving a fineness of deposit not heretofore attained by any other means. The very nature of his solvent prevented him from observing any solvent action on the pyroxylin due to the presence of camphor, and nobody in his senses will be rash enough to assert that this disclosure of Cutting constitutes the invention of the pyroxylin-camphor compound.

We find the next mention of camphor in the British Patent "MANUFACTURE OF COMPOUNDS OF PYROXYLIN" No. 1313, of May 11, 1865, of Alexander Parkes, Birmingham, the one which the romancers rely on when they try to rob Spill of the credit due him. Parkes mentions in this specification four solvents of low volatility, anilin, nitrobenzol, glacial acetic acid, and camphor, the latter only casually. The three former are specifically enumerated in his claim, but camphor is omitted, a point of significance to any one familiar with patent matters, especially in view of the fact that Parkes and Spill were associates. There is not a word in either this or any other of Parkes' patents that directs the joint use of absolute alcohol and camphor, as has been deduced by some from the famous decision (rendered August 21, 1884) which held Spill's U. S. Patent of November 30, 1869, invalid. In No. 1313 Parkes recommends, as he does elsewhere, absolute wood alcohol or what he conceives to be such; and in his British Patent No. 2675 of October 28, 1864, "PREPARING COMPOUNDS OF GUNCOTTON AND OTHER SUBSTANCES," he states that alcohol, treated in an analogous manner, may be substituted for wood alcohol. Now both of these alcohols gelatinize pyroxylin, so the dissolving power of camphor was not disclosed. Spill, who was a keen observer, noted that it was possible to use moist pyroxylin, as may be gathered from several of his patents, and drew the conclusion that in certain combinations the employment of anhydrous alcohols was not essential. In his British Patent No. 2,666 of September 21, 1867, "TREATING XYLOIDINE," he gives us the important solvent commercial grain alcohol mixed with benzol. Two years later, British Patent No. 3,102 of October 26, 1869 and U. S. Patent 97,454 of November 30, 1869, he published

his famous formula of a solution of camphor in commercial grain alcohol, and this formula and this disclosure are and have been the foundation of the celluloid industry. Spill's process of gelatinizing pyroxylin by means of this solvent and masticating the pasty mass between rolls is and has been the process followed by celluloid manufacturers all over the world, Hyatt and his backers included, and not the visionary, inoperative process of U. S. Patent 105,338 of July 12, 1870, granted to John W. Hyatt, Jr., and Isaiah S. Hyatt. The patent covering this alleged invention was several times re-issued, exalted to the state of a fetic, and made an instrument of the most oppressive patent litigation. Hyatt disclaims the use of alcohol, but in practice cannot do without it. What his actual knowledge was, is best evidenced by this quotation from the text of 105,338:

"The product is a solid about the consistency of sole leather, but which subsequently becomes as hard as horn or bone by the evaporation of the camphor. Before the camphor is evaporated the material is easily softened by heat, and may be molded into any desirable form, which neither changes nor appreciably shrinks in hardening.

"We are aware that camphor made into a solution with alcohol or other solvents of camphor has been used in a liquid state as a solvent of xyloidine. Such use of camphor as a solvent of pyroxylin we disclaim."

In passing, I may remark that the step of the first claim "Grinding pyroxylin into a pulp" was published in British Patent No. 2,249 of September 15, 1860, granted to Stephen Barnwell and Alexander Rollason.

That Hyatt experienced great difficulty in circumventing Spill's patents and in fact did not succeed, does not constitute him the inventor of the pyroxylin-camphor compound which Spill first made, and which is made to-day by Spill's original method.

The decision that the step taken by Spill was too short to entitle him to a patent may have appeared very obvious in 1884, especially to his rivals, but I am of the opinion that it was a tremendous leap forward in 1869. But whichever way one may view this decision, it does not establish that Hyatt was the inventor of celluloid, the material, not the trade mark, nor that Hyatt's process is the one used in the industry. Rather the reverse, it says that anybody may use Spill's process, Hyatt's backers, the defendants in this suit, included.

Considering the exceptional opportunities which Prof. Chandler has enjoyed to acquaint himself with the real processes and the history of the celluloid industry, nothing could be less defensible than the use he tries to make of Spill's British Patent 1,739, of May 11, 1875. For the benefit of unbiased readers, I append herewith a circular of the Xylonite Company, Limited, bearing date of March 31, 1871, which shows better than anything else what had been accomplished at that early date:

### THE XYLONITE COMPANY LIMITED

MANUFACTORY HACKNEY WICK, LONDON, N. E.  
Mr. D. Spill, Manager

XYLONITE: a substitute for Ivory, Bone, Horn, Tortoise-shell, Hard Woods, Vulcanite, Papier Maché, Marbles, Brass, and Veneers for Cabinet Work. It is also applied to Waterproofing Fabrics, Leather, Cloth, Book Binders' Cloth, Card Cloth, Writing Tablets, Bagatelle Balls and Pianoforte Keys, Gear and Friction Wheels, and Bearings for Machinery, Spinner's Bosses, Tubing; and as an Insulator and protector of Telegraph Wires.

It may be embossed, turned, polished, and worked in the same manner as the substances above named; is not affected by chemicals, or atmospheric changes, and is, therefore, valuable for shipment to hot climates.

It is also applicable to Photographic purposes, viz., as windows for the Dark Room, for which the material is chemically prepared so as to arrest the actinic rays of light. It can also be spread upon fabrics for the purpose of Field Tents, thus avoiding the use of colored glass windows; and lastly, differently prepared, is a substitute for glass plates for Negatives, it having

<sup>1</sup> THIS JOURNAL, 6 (1914), 156-158.

the advantages of being light, flexible, and durable, and perfectly structureless.

#### INSTRUCTIONS TO SURFACE AND POLISH XYLONITE SHEET

The Surface of the sheet can be made smooth with either a file, glass paper, scraper, or plane; or by grinding on a stone, either with fine emery powder and water, fine emery powder and oil, or pumice stock and water; it may also be pressed to a smooth surface between polished plates of metal heated to about 212 degrees Fahrenheit.

Polish with oil and crocus, oil and rotten-stone, or oil and whiting, combined with friction; it may also be French polished, in the same manner as cabinet work or hard woods.

The friction polish is most durable, and may be obtained by the use of a rotary wheel or oscillating flat plate, having a leathern or woollen surface well supplied with the above-named polishing powders, combined with oil or water. Finish with a rotating or oscillating brush or wheel made of hair, cotton or wool, well supplied with whiting combined with oil or water.

#### INSTRUCTIONS FOR WORKING AND FASTENING HANDLES

To work Xylonite Handles for Table or Pocket Cutlery, the material should be first surfaced or shaped, either with a hardened steel file, or by grinding upon "fine grit" stones, supplied with water in any convenient way; then polished on a leather surfaced or buff wheel, well supplied with rotten-stone and oil, or powdered pumice stone, and oil; and finished on a rotating dolly or wheel composed of hair, cotton, woollen rays, or felt, well supplied with whiting combined with oil or water. This will give a high gloss, similar to ivory.

In many instances the ordinary method of polishing ivory will suffice.

Previous to working Xylonite into Table or Pocket Knife Handles, in large practice, it is desirable, in order to avoid the possibility of the warping or contortion of the material, that the article should be shaped approximately to its finished form, either by file or grinding; the hole drilled for the tang; and the rough handle then seasoned and set, by exposing it for from 14 to 21 days to a warm and free atmosphere of about 100 to 130 degrees Fahrenheit. After this it may be surfaced and polished.

Xylonite may be moulded into form under combined pressure and heat. The mould and material should be heated to about 212 degrees Fahrenheit, pressure then applied, and the mould allowed to remain until cool, or it may be plunged instantly into cold water, in order to set the shape quickly.

To permanently fasten Xylonite Handles, which will not be affected by climate or boiling water, and do not require pinning or riveting:

Heat the tang of the blade in a gas flame to about 300 degrees Fahrenheit, or, say a blue heat.

Fill the drill hole of the handle with flour of sulfur or powdered brimstone, then insert the hot tang; this will melt the powder, the excess of which will escape while adjusting the handle; in a few seconds the tang will be sufficiently cool for the handle to become firmly set. Half a dozen tangs may be heated at one time by an ordinary gas flame at the workman's bench in about one minute, thus economizing time, avoiding the inconvenience and risk of fires, and the use of the melting pot.

If necessary to remove handles from the tang, hold the blade firmly in a vice, then with a lever or spanner forcibly twist the handle round, at the same time pulling it off; this may be executed without injury to the article.

Knives having Xylonite handles fastened as above described may be cleaned with boiling water without risk of becoming cracked, discolored, loose on the tang, or injured in any way, as neither the material nor the fastening will be affected by heat considerably above the temperature of boiling water.

The ordinary fastenings with Rosin will not answer with Xylonite handles.

7, GREAT WINCHESTER STREET BUILDINGS, E. C.  
LONDON, 31st March, 1871

#### GENTLEMEN:

I beg to inform you that this Company has appointed Messrs. BEACH & Co., of Hartford, Connecticut, the sole Agents for the United States of America and Canada.

You will, therefore, oblige by forwarding to them your orders for the future, which will receive prompt attention.

Messrs. Beach & Co. will have the pleasure of affording you full particulars of the various uses of our material, together with Price Lists, etc.

I am, Gentlemen, Yours obediently,

HERBERT J. CANNING, Secretary

Tons of Spill's xylonite were at this time imported into this country. Worden's description ("Nitrocellulose Industry," pp. 571, 572) of Spill's work is incomplete. His criticism of Parkes' processes (*Ibid.*, p. 568, foot-note) does not tally with the facts.

In regard to the dehydration of pyroxylin by means of alcohol, Mr. Hyatt labors under a misapprehension. This process is about as old as collodion itself, and was first patented by Cutting in 1845. It was first employed in an industrial way by J. R. France, the late President of the Arlington Company (died in 1895), and when his company was sued for infringement

of the Hyatt alcohol dehydration patent, it took only one hearing to cause a discontinuance of the suit.

The invention of celluloid has been discussed<sup>1</sup> before in a manner sufficiently lucid to cause anybody not possessed of the light-heartedness of Prof. Chandler and Dr. Baekeland to make a little more sure of his premises. I think I gave Mr. Hyatt due credit in the article which Prof. Chandler takes exception to, as I also did in 1895, when I said:

"In the United States, J. A. McClelland and John W. Hyatt were at work to utilize the valuable properties of soluble pyroxylin. But an invention overshadowing all the others in importance was made by Daniel Spill in 1869, when he first produced a pyroxylin-camphor composition, plastic at about 75° C., by gelatinizing pyroxylin by means of a solution of camphor in commercial grain alcohol. As far as the chemical side is concerned, Daniel Spill must be hailed as the father of the celluloid industry, while to John W. Hyatt, at that time of Albany, N. Y., the greatest credit is due for devising suitable machinery for the intricate processes involved, for discerning the importance of pure materials, and for the perseverance which he exhibited under most adverse conditions."

It would have been much better to have the presentation of the Perkin medal to Mr. Hyatt based on the things which he accomplished, of which there are a good many.

ROBERT C. SCHÜPPHAUS

175 PEARL STREET, NEW YORK  
March 27, 1914

#### LABORATORIES IN THE CHEMISTS' BUILDING

The Chemists' Building Company, organized primarily to finance the construction and operation of a building in which to house The Chemists' Club and various Chemical Societies in New York City, starts on May 1st next, a new form of leases for its tenants.

There has been a good demand for laboratories in the Chemists' Building and only a few of them are left. They rent at a uniform rate of \$2.00 per square foot per annum. Each laboratory has its own gas supply and meter. Heat, electric light, water, compressed air and vacuum are supplied by the building. Laboratories have openings for hood connections. The Chemists' Building is most conveniently located at 50 E. 41st Street close to the Grand Central and Subway Stations.

The Chemists' Club acts as agents for the Building Company, and all inquiries may be addressed to the House Committee or the Superintendent of the Club.

#### AN INVESTIGATION OF THE PRESENCE OF FURFURAL IN CIDER VINEGAR—A CORRECTION

Through an oversight the final paragraph of the article under the above title in THIS JOURNAL, 6, 214, was omitted. It follows: "The vinegars used above, except the farmers' vinegars, were made under the direction of Asst. Prof. H. Louis Jackson for his study of pure cider vinegar. The test for furfural was made at his suggestion."

AGNES A. ANDERSON

STATE FOOD LABORATORY  
UNIVERSITY OF KANSAS, LAWRENCE  
April 13, 1914

#### CORRECTION

The articles on "Sociological Work of the New Jersey Zinc Company" by F. Hughes, "Welfare and Safety Provisions at the Welsbach Company's Plants" by H. Lyon, THIS JOURNAL, 6, 333 and 336, were presented at the JOINT MEETING of the New York Sections of the American Chemical Society, The Society of Chemical Industry and the American Electrochemical Society, Dec. 12, 1913, and not at the Annual Meeting of the American Institute of Chemical Engineers as stated in the foot-notes.

<sup>1</sup> Schüpphaus, *Jour. Soc. Chem. Ind.*, 14 (1895), 557 and 26 (1907), 383; Joyce, THIS JOURNAL, 3 (1911), 194 and 702.



## PERSONAL NOTES

Sir Ernest Rutherford, F.R.S., of the University of Manchester, England, spoke before the National Academy of Sciences, April 21st, 22nd and 23rd on "The Constitution of Matter and the Evolution of the Elements." This is the beginning of a series of lectures covering several years and designed to give a clear and comprehensive outline of the broad features of inorganic and organic evolution in the light of recent research. The expenses of this series are taken care of by the William Ellery Hale Foundation, made in memory of the late William Ellery Hale of Chicago.

The Columbia University Commencement this year takes the form of a celebration of the 50th Anniversary of the founding of the School of Mines. An especial feature will be the Inauguration of the Chandler Lectureship and the Award of the Chandler Medal on May 29th. The first Chandler Medal will be awarded to Dr. Leo. H. Backeland.

A portrait of Sir William Ramsay, painted by Mr. Mark Milbanke, has been presented to University College, London, by former colleagues and past students. Prof. J. Norman Collie made the address. A replica of the portrait has been presented to Lady Ramsay.

The Pratt Institute Chemical Alumni Association of Brooklyn held their 16th Annual Reunion and Dinner at the Hotel Gregorian on the evening of April 16th. The dinner was well attended and brought together graduates of the three-year evening course for the last eleven years. Reports from various members showed that many responsible positions are being filled by graduates of the Institute. Arthur S. Somers acted as Toastmaster. Dr. W. R. Whitney of the General Electric Co. talked interestingly on the research that led up to the production of the metal filament incandescent lamp. Dr. S. G. Rogers, Medical Inspector of the N. Y. State Department of Labor, told how they were trying to render labor more efficient by improving sanitary conditions. Other speakers were: District Attorney James C. Cropsey of Kings County, Geo. A. Hitchcock, Samuel S. Edmunds of Pratt Institute and Arthur F. Wiehl. All the past presidents of the Association were seated at the head table with the guests of the evening. The officers for the coming year are: Arthur F. Wiehl, *President*; Harry W. Lange, *Vice-President*; Irving A. Schumann, *Secretary-Treasurer*; A. J. Farry, Harry J. Bloom, Wm. J. Bedell and G. Clarence Woolley, *Directors*.

Dr. Max A. Kunkler, research chemist for The Joslin-Schmidt Co. of Cincinnati, died March 29th at the age of 26.

On March 28th the members of the "Round Table" at the Bearon Café, New York City, gave a luncheon to their honored member, Adolf du Faur, commemorating the 88th anniversary of his birth. Chemists, Mining Engineers, Metallurgists and Chemical Merchants meet daily for luncheon at the "Round Table" which is known the world over. The luncheon was under the direction of Dr. Hugo Schweitzer, who, in the name of the "Stammtisch," delivered an address of congratulation in German. Dr. Emil Schill then presented Mr. du Faur with an engrossed certificate of honorary membership (the first awarded) in the N. Y. Section of Verein Deutscher Chemiker. Mr. du Faur responded, acknowledging his pleasure at the honor accorded him. Among those present were: F. A. Schütz and F. F. Schütz, Jr., son-in-law and grandson of Mr. du Faur; Emil Schill, E. A. Widmann, H. C. A. Seeborn, H. Lieber, T. J. Parker, T. B. Wagner, E. Bilhuber, F. Stobaues, Aston and Karl Eilers, Mr. Fohr, Willard P. Ward, Theo. Geisenheimer, Carl Beckmann, H. C. Schüpphaus, Bernhard C. Hesse, L. Saarbach, F. de Jahn and many others.

Mr. Faber du Faur was born March 27, 1826 in Wasseralfingen, Württemberg. He attended the Polytechnicum in Stutt-

gart and studied chemistry under Fehling. His faithfully kept college diary was presented by him to the Library of The Chemists' Club. He landed in the United States, Jan. 1, 1851, where as a Mining Engineer and Patent Attorney he has led an active and eventful life. Among his numerous inventions, for which he was granted valuable patents, the Tilting Furnace, invented in the early sixties and still in common use deserves especial mention. During the Civil War, he served as Adjutant to General Meigs and as Captain of Engineers was entrusted with the task of fortifying and defending Washington.

Dr. N. Edward Loomis, Assistant Professor of Chemistry at Bowdoin College, Brunswick, Maine, has recently been called to take charge of the newly organized Department of Physical Chemistry at Purdue University, Lafayette, Indiana.

G. H. P. Lichthardt, Analyst of the Sacramento Department of Health, calls attention to a new adulterant which he has found in Ice Cream Cones. These yielded 0.50 and 0.45 per cent of strongly alkaline ash which had a silica content of 50 and 47 per cent. Inspection of the manufacturing plant showed that water glass solution was being used, acting, no doubt, as a preservative and allowing the use of a thin batter in making up the cones.

On April 15th, the reorganizers purchased the property of the American Water Works & Guarantee Co. at the receiver's sale. The consideration was \$1,250,000.

The Connellsville, Pa., coke production, which has been around 350,000 tons weekly, is being materially curtailed. During the middle of April, the Frick Company closed 1,300 ovens, and it was reported that other interests had shut down many ovens. The number of ovens in operation for an output of 350,000 tons per week (9,700 cars) is 27,000.

The Itinerary of the Annual Chemical Inspection Trip for Advanced Chemistry and Chemical Engineering Students of the University of Illinois included visits to the following plants in and near Chicago: Universal Portland Cement Co., Buffalo, Ind.; Indiana Steel Company; The By-Product Coking Plant; Illinois Steel Co.; Standard Oil Refinery, Whiting, Ind.; Grasselli Chemical Co.; U. S. Metals Refining Co.; American Smelting & Refining Co.; Sherwin-Williams Co.; Armour & Co. Soap Works; Peoples' Gas, Light & Coke Co.

The American Manganese Manufacturing Co., which is in possession of a large deposit of manganese ore in Minnesota, proposes to produce ferro-manganese at the plant of the Dunbar Furnace Co., Pittsburgh, Pa.

Sir Ernest Rutherford of Manchester, England, lectured on "Recent Advances in Radioactivity" on April 18th under the auspices of the Columbia University Department of Physics. In substance the lecture was the announcement of the following conclusions drawn from recent experiments as yet unpublished: (1) Absolute proof that the  $\alpha$ -particles projected from radioactive substances are helium atoms. (2) Experiments studying the scattering of the  $\gamma$ -rays by matter show that positive electrons are excessively concentrated, even more so than the negative ones. (3) The charge on the nucleus of an atom is proportional to the atomic weight of the element. (4) Study of the "magnetic spectra" of radioactive elements indicates that the escape of  $\beta$ -particles from the nucleus of an atom starts a radiation that is the  $\gamma$ -radiation and that is the characteristic mode of vibration of that particular kind of atom. (5) Further studies of the  $\gamma$ -radiation lead to the conclusion that the charge on the nucleus of an atom controls its properties; *i. e.*, that elements of different atomic weights may have identical properties, *e. g.*, Radium B and lead have the same "magnetic spectrum" as reflected from rock salt crystals.

# GOVERNMENT PUBLICATIONS

By R. S. McBRIDE, Associate Chemist, Bureau of Standards, Washington

**NOTICE.**—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate. Consular Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington. The regular subscription rate for these consular reports mailed daily is \$2.50 per year, payable in advance, to the Superintendent of Documents.

## HOUSE OF REPRESENTATIVES

**Radium.**—Report from Committee on Mines and Mining favoring House Bill No. 12741, which is intended "to provide for and encourage prospecting, mining, and treatment of radium-bearing ores in lands belonging to United States, for purpose of securing adequate supply of radium for government and other hospitals in United States," dated February 3, 1914. (18 pages; paper, 5c.) In this connection House Joint Resolutions 185 and 186 and Senate Bill 4405 and the hearing reports on them, are of interest. These latter are not published for general distribution, but can be secured from members of Congress in some cases.

## STATE DEPARTMENT

**Transactions of 15th International Congress on Hygiene and Demography.** Edited by the Secretary General. 6 Vols., 9 parts. Complete report, with accompanying papers, of the sessions held in Washington, D. C., September 23–28, 1912. Not available for general distribution. Of value to those interested in hygiene, sanitation and allied subjects.

## PATENT OFFICE

**Official Gazette.** Weekly publication for sale by Superintendent of Documents, \$5 per year or 10c. per copy, in advance. Reports all patents granted and court decisions on patent cases; lists trademarks, designs, labels and prints at time when filed with office and announces their subsequent registration, when listing and registration are not simultaneous.

**Classification Bulletin.** 16 pp. Paper, 10c. Revised classification of subjects of invention, prepared by Classification Division for July 1 to Dec. 31, 1913.

## BUREAU OF THE CENSUS

**Report of the 13th Census. Volume X—Manufactures.** 975 pp. Cloth, \$1.25. The statistics of manufactures for certain selected industries were published as separate bulletins as rapidly as the statistics were compiled. These bulletins are now collected in the present volume, which is one of the eleven volumes constituting the full report of the 1910 census. The report for each industry gives data from operations in the calendar year 1909 of all establishments operating under the factory system, excluding "neighborhood, household, and hand industries." Some of the major classifications of the industries of chemical interest are the following: Textiles; metallurgical; electrical machinery and supplies; packing-house; dairy; canning; milling; starch and glucose; manufactured-ice; salt; sugar; general chemical and allied; bone, carbon, and lamp-black; dyestuffs; explosives; fertilizers; essential oils; acids; wood distillation; coke; gas; petroleum; soap; turpentine and rosin; leather; paper and pulp; clay products; and glass.

The large mass of data prevents review of the material presented; in general, there are statistics given on the following phases of each subject: General statistics, summary by geographical location, character of ownership, size of establishments, number of persons engaged, expenses, character of supplies and products, and values of each.

Data are given in detail for each state in addition to general summaries, and statistics for the metropolitan districts are also separately reported.

Separate bulletins are available in some cases, or the full set of reports may be consulted at libraries. An "Abstract of the Census" has also been prepared which is more convenient for general use. The section on *chemicals and allied industries* (other than those particular ones listed above) is obtainable as a separate paper for 15 cents.

**Report of the 13th Census. Volume XI—Mines and Quarries.** 369 pp. Cloth 65c. Statistics for mines and quarries similar to those outlined above for manufactures, being a general report and analysis. The most important mineral products are shown to be as follows, in order of value of product for year 1909: Bituminous coal, natural gas, anthracite coal, iron, copper, precious metals, limestone, lead and zinc, granite and trap-rock, sandstone, phosphate-rock, marble, slate, gypsum, sulfur and pyrite, clay, talc and soapstone, and mercury.

In addition to general summaries, there are detailed figures for each state; and elaborate reports on coal, iron, petroleum and natural gas are included.

## INTERNAL REVENUE COMMISSIONER

**Alcohol.** Several reports and decisions on alcohol have appeared recently from this office, as follows:

*Regulations and instructions relating to manufacture, redistillation and denaturation of domestic alcohol.* Regulations 30 revised, supplement 2. 16 pp. Paper 5c.

*Denatured alcohol*, formula 2B, for especially denatured alcohol for use in manufacture of pyroxylin plastics. Treasury decision 1954. 4 pp.

*Use of Mash fit for distillation* in production of artificial wines. Treasury decision 1949. 2 pp.

## GEOLOGICAL SURVEY

**List of Publications.** Circular No. 15 of the Superintendent of Documents office gives a recently revised list of all publications of the Survey.

**Contributions to General Geology.** Certain "professional papers" will each be made up of a number of short articles, and will form a series under the above title. The first of this series of articles are just out, published as separates from Professional Papers 85 and 90; the following two are included:

**Resins in Paleozoic Plants and in Coals of High Rank.** By DAVID WHITE. Professional Paper 85-E, 32 pp. Evidence is presented that anthracite and bituminous coals, as well as those of lower rank, originated as peats and in certain cases from resin-bearing plants. The significance of the relative resin content of coals is pointed out.

**Geology of the Pitchblende Ores of Colorado.** By E. S. BASTIN. Professional Paper 90-A. 5 pp. A brief account of the occurrence of radium-bearing minerals in this district is given advance publication in this paper.

**Mineral Resources of the U. S., Calendar Year 1912. PART I, METALS.** 1079 pages; PART II, NONMETALS, 1218 pp. Statistics of the production, importation, and exportation of mineral substances in the United States, including accounts of the chief features of mining progress, comparisons of past and present production and conditions, and the application of the products in the useful arts. A consolidation of 63 advance chapters, each covering a single mining industry or group of allied industries. Among the chapters of chemical interest are those on: Abrasives; borax; gypsum; magnesite; phosphates; salt and bromine; bauxite and aluminum; gas, coke, tar and ammonia; precious and semi-precious metals (in several special districts).

**Contributions to Economic Geology, 1912. PART I, METALS**

AND NONMETALS EXCEPT FUELS. Bulletin 540. 563 pp. This bulletin is made up of 30 brief reports on such investigations of mineral deposits as have a direct economic bearing; separate copies of the reports are available in most cases. Topics of pure geological or mineralogical interest are not taken up. Each report deals with certain minerals or ores for one district only. Among the subjects so treated are: deposits of gold, copper, lead-silver, iron, titaniferous magnetite, alunite, granite, marble, clay, phosphates, potash and other salines, salt and borax, sodium sulfate, borates, niter, sulfur, magnesite, celestite, and diamond-bearing peridotite.

PART II, FUELS. Bulletin 541. This section is not yet complete, although some separates have appeared.

#### BUREAU OF MINES

**Fuel Briquetting Investigations, July, 1904 to July, 1912.** By C. L. WRIGHT. Bulletin No. 58, 277 pp and 21 plates. Paper 45c. This bulletin reports the results of fuel briquetting begun under the U. S. Geological Survey in 1904 and continued at various places until July, 1912. Results previously reported in government publications as well as new information are assembled in the present bulletin. The condition of the briquetting industry, costs, machinery used, and fuels available for use in this work are discussed. A large amount of tabular data are given, including: results of analyses, physical tests and combustion experiments on the fuels, binders and briquets of different sorts. Detailed data for many coals and lignites are reported.

**The Sampling and Examination of Mine Gases and Natural Gas.** By G. A. BURRELL and F. M. SEIBERT. Bulletin No. 42, 116 pp. and 2 plates. Paper 20c. The subject matter is arranged under principal headings among which are the following: Collection of samples of mine gases; determination of moisture; apparatus and methods used (for air analysis, determining  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{H}_2$ ,  $\text{N}_2$ , and  $\text{CH}_4$ ); apparatus used in analyzing other gas mixtures (such as illuminating gases); detection of carbon monoxide (by mice and birds); determination of oxides of nitrogen in mine air; use of the gas interferometer; and apparatus for analyzing natural gas. A large amount of old material is included from former reports of this Bureau and other sources, but experimental results from recent work and extended discussion of the various methods are also given. Much of the material would be of value to a person interested only in artificial gas or air analysis, both in regard to apparatus and methods.

**Petroleum Technology.** A new sub-series in the bulletins of this Bureau is given this title; this sub-series is made up, as is the sub-series on "mineral technology," of bulletins numbered serially as a part of the full list of the bulletins.

**Permissible Explosives.** By CLARENCE HALL. Technical Paper No. 71. 12 pp. Paper 5c. A list of all explosives found by tests previous to January 1, 1914, to conform to rules of the Bureau of Mines. (See earlier publications of this Bureau for full reports on methods of testing and proper storage and handling.)

**Metal-Mine Accidents.** Compiled by A. H. FAY. Technical Paper 61. 74 pp. Paper, 10c. Classified statistics for operations of 1912, showing causes and distribution (both geographic and by character of mine) of accidents.

**Mud-laden Fluid Applied to Well Drilling.** By J. A. POL-LARD and A. G. HIGGIN. Technical Paper 66. 20 pp. A proposed method for gas and oil-well drilling is described, by which wells may be drilled and the oil recovered without waste of the gas which accompanies it. This is an important matter where gas is struck when there is immediate commercial demand only for oil.

**Production of Explosives in the U. S.** Compiled by A. H. FAY. Technical Paper 69. 7 pp. The total production of explosives during 1912 was reported as follows:

	POUNDS
Black Powder	230,233,369
Permissible explosives	24,630,270
"High" explosives (dynamite nitroglycerine, dynalite, gun cotton, etc.), other than permissible explosives	234,469,492
TOTAL	489,333,131

The locality and purpose of use are shown by full data; utilization is accompanied by an average of 0.59 fatalities per 1,000,000 lbs. of explosive used.

**Relative Effects of Carbon Monoxide on Small Animals.** By G. A. BURRELL, F. M. SEIBERT and I. W. ROBERTSON. Technical Paper 62. 23 pp. Paper 5c. Of value in study of mine-accident prevention.

#### BUREAU OF STANDARDS

**Copper Wire Tables.** Circular No. 31, 2nd Edition. 70 pp. This circular with its tables was prepared at the request and with the cooperation of the standards committee of the American Institute of Electrical Engineers. The data on which the tables are based were formally adopted as international copper standards by the International Electrotechnical Commission in September, 1913. Tables, accompanied by full discussion, give the resistivity, temperature coefficient and density of annealed copper, comparison of wire gages, data for copper-cable and aluminum-wire resistivities, etc.

**Testing of Barometers.** Circular No. 46. 12 pp. The characteristics of barometers suitable for various uses are given, and the limitations of each type briefly indicated. A description is included of the tests made by the Bureau of Standards in the calibration of mercury or aneroid barometers and instructions are given regarding application for tests and fees charged. The fees vary from \$10 for a determination of the gas correction or a calibration with high accuracy, to \$2 for test at one point on a common barometer with ordinary accuracy. Fees for tests on aneroids vary with character of test and number of instruments submitted.

**The Testing of Mechanical Rubber Goods.** Supplement to Circular of this name, which is No. 38. 16 pp. Preliminary report and recommendations of Joint Rubber Insulation Committee for specifications for rubber compounds and for the procedure for analysis of rubber compound. These specifications are adopted as tentative for one year's trial by the Committee. A model specification for 30 per cent Hevea rubber compound is also proposed in preliminary form. (The original circular No. 38 deals largely with the processes of manufacture and mechanical testing of rubber goods.) (See THIS JOURNAL, 6, 75.)

**Testing of Hydrometers.** Circular 16, 3rd edition. 16 pp. A revision of the Bureau's hydrometer specifications, instructions for the use of hydrometers, description of methods and statement of fees for testing them.

**Standard Specifications for Incandescent Electric Lamps.** Circular 13, 6th edition. 20 pp. Revised specifications used by the U. S. Government in lamp contracts and proposed as suitable for general use by other purchasers.

**Bulletin, Vol. 9, No. 4, and Vol. 10, Nos. 1 and 2** have come from press since January 1st. These include the following scientific papers, each of which are obtainable as separates:

(1) **A Micropyrometer.** By G. K. BURGESS. Scientific Paper 198. 4 pp. The microscope and pyrometer used for melting-point determinations on minute specimens of metals, etc., are combined in one instrument to enable a single observer to watch the melting and to make the temperature measurement.

(2) **Melting Points of the Refractory Elements. I—Elements of Atomic Weight from 48 to 59.** By G. K. BURGESS and R. G. WALTEBERG. Scientific Paper 205. 14 pp. Micro-pyrometric measurements of the melting points in hydrogen of these elements gave the following results: Ni  $1452 \pm 3$ ;



Co 1478 = 5; Fe 1530 = 5; Mn 1260 = 20; Cr 1520 to greater than Fe; Va 1720 = 20; and Ti 1794 = 12.

(3) **Simplified Formula for the Change in Order of Interference Due to Changes in Temperature and Pressure of Air.** By I. G. PRIEST. Scientific Paper 199. 4 pp.

(4) **New Calorimetric Resistance Thermometers.** By H. C. DICKINSON and E. F. MUELLER. Scientific Paper 200. 10 pp. A new form of electrical resistance thermometer having small lag and numerous advantages for use in high precision calorimetric work.

(5) **The Silver Voltameter. Part III.** By E. B. ROSA, G. W. VINAL and A. S. McDANIEL. Scientific Paper 201. 60 pp. Reports the second series of quantitative experiments and the preparation and testing of silver nitrate for this work. (Previously abstracted in C. A.)

(6) **Note on Cold-Junction Corrections for Thermocouples.** By P. D. FOOTE. Scientific Paper 202. A discussion of the importance and method of making this correction; omission of the correction may cause errors as great as 50° C.

(7) **Latent Heat of Fusion of Ice.** By H. C. DICKINSON, D. R. HARPER 3d, and N. S. OSBORNE. Scientific Paper 209. 31 pp. Measurements by two independent methods in a precision calorimeter on 92 samples of 100 to 500 grams of ice from various sources give results agreeing within 1 part in 1000. The mean of the final 21 determinations on samples of "plate," "can" and "natural" ice gave for the latent heat of fusion 79.63 calories (15°) per gram mass, equivalent to 143.3 B. t. u. per pound mass or to 143.5 B. t. u. per pound weighed in air against brass or iron weights.

(8) **Melting Points of Some Refractory Oxides.** By C. W. KANOLT. Scientific Paper 212. 18 pp. Measurements in a graphite resistance furnace, using an optical pyrometer; the results reported are as follows:

Oxide	M.P.	Supporting material
Cr <sub>2</sub> O <sub>3</sub>	1990°	Tungsten, graphite
Al <sub>2</sub> O <sub>3</sub>	2050°	Tungsten, graphite
CaO	2572°	Tungsten, CaO
MgO	2800°	Graphite

**Special Studies in Electrolysis Mitigation.** By E. B. ROSA and B. MCCOLLUM. Technologic Paper 27. 55 pp. A report on the preliminary study of conditions in Springfield, Ohio, with recommendations for mitigation. The results are presented for this one case, but the principles laid down can be taken as of general interest and value.

**Viscosity of Porcelain Bodies.** By A. V. BLEININGER and PAUL TEYTOR. Technologic Paper 30. 11 pp. As a measure of viscosity the deformation under tensile strain was used at temperatures from 1060° to 1310°. Tabular results and curves are given.

#### DEPARTMENT OF AGRICULTURE

**Agriculture Bulletins.** Publications of bulletins and circulars by the bureaus of the Department of Agriculture has been discontinued; all such contributions (from bureaus of Chemistry, Soils, Animal Industry, Plant Industry, etc.) will hereafter be published in the new series of Bulletins issued from the office of the Secretary of Agriculture and called "Agricultural Bulletins."

**Journal of Agricultural Research.** Monthly, free only to certain libraries and institutions generally on exchange. Annual subscription price \$2.50 per volume of 12 numbers, payable in advance to the Superintendent of Documents. The numbers of this year have thus far contained the following articles of chemical interest:

(1) **Environmental Influences on the Physical and Chemical Characteristics of Wheat.** By J. A. LEClerc and P. A. YODER.

(2) **Presence of Some Benzene Derivatives in Soils.** By EDMUND C. SHOREY.

(3) **Crystallization of Cream of Tartar on Fruit of Grapes.** By WILLIAM B. ALWOOD.

(4) **Reduction of Arsenic Acid to Arsenious Acid by Thiosulfuric Acid.** By ROBERT M. CHAPIN.

**A Special Flask for the Rapid Determination of Water in Flour and Meal.** By JOHN H. COX, Asst. in Grain Standardization, Bureau of Plant Industry. Agricultural Bulletin 56. 7 pp. Paper 5c. Simple description and directions for use of this flask in flour and grain testing.

**Tests of the Waste, Tensile Strength, and Bleaching Qualities of the Different Grades of Cotton.** By N. A. COBB, Agricultural Technologist, Bureau of Plant Industry. Agricultural Bulletin 62. 8 pp. Paper 5c. A preliminary report on milling tests of interest in cotton-mill work.

**Manufacture of Flavoring Extracts.** By E. M. CHACE. Reprint (new edition) from yearbook of 1908. 10 pp. Paper 5c.

**Respiration Calorimeter and Results of Experiments with It.** By C. F. LANGWORTHY and R. D. MILNER. Reprint (new edition) from Yearbook of 1910. 12 pp. Paper 5c.

**Giant Kelps of the Pacific Coast as a Source of Potassium Salts.** By F. K. CAMERON. Bureau of Soils. An extended report on this subject is ready for press; it will be accompanied by maps of the kelp beds and includes recommendations as to the utilization of the new source of potassium for use as a fertilizer.

**List of Publications.** Circular 40 of Superintendent of Document Office is an alphabetical subject list of the bulletins and circulars of the Bureau of Chemistry and of the published proceedings of the annual conventions of the A. O. A. C., so far as they are now in stock.

**Methods of Food Analysis.** This Bulletin (No. 107 of Bureau of Chemistry), which gives the official and provisional methods for food analysis of the A. O. A. C., will be revised within a year; but another reprint of the current edition has been made and copies are to be had from the Superintendent of Documents for 20c.

#### CONSULAR REPORTS, MARCH

**Ramie Fiber and its Manufacture.** Description of the cultivation and manufacture of ramie fiber in China and Cuba and of the experiments toward its production in the Philippines. This material is mostly used for making "grass cloth" and paper, especially banknote paper. On account of its strength and resistance to moisture, ramie fiber is being used in one English factory as a substitute for hemp and flax. (Pp. 801-9.)

**Alum Production of Shabin Kara Hissar.** From 2000 to 3000 tons of alum are produced annually from natural deposits near this Turkish town. (P. 812.)

**A new Cement Factory,** with an annual production of 800,000 barrels is about to be erected in the Gori district of the Caucasus. (P. 825.)

**Mineral Oil and Natural Gas** have been reported from Marvaor, Nyitra County, Hungary. (P. 827.)

**Iron Ore** shipments from Korea in 1913 amounted to 135,263 tons, an increase of 3,000 tons over 1912. (P. 846.)

**A Soap and Candle Factory** started operations at Panama on Feb. 1, 1914. (P. 846.)

**A Seed-Oil Clearing House** has been established in Liverpool. (P. 875.)

**Tests of Para Rubber-seed Oil and Cake** showed that the oil has drying properties inferior to those of linseed oil and is not suited to the manufacture of linoleum, but can be used in making soft soap. Feeding experiments showed that the seed cake is suitable for feeding cattle, but not sheep. (P. 854.)

**Colored Oil for Oleomargarine** may be made from palm oil, which, when carefully prepared, has a high melting point (75°-100° F.) and has no disagreeable taste. (P. 875.)

**The Sulphate of Ammonia** industry in Germany produced 500,000 metric tons in 1912, and 418,000 metric tons in 1911. Owing to competition between manufacturers in Bochum and in Ludwigshafen, the price is likely to decrease. (P. 878.)

**Petroleum Fields** in Bolivia are likely to be developed soon by two syndicates. (P. 879.)

Experiments on **Electric Sparks and Mine Explosions** in Wales, showed that sparks from a line at 9 volts (used in signaling) could not ignite an explosive atmosphere. (P. 879.)

**Cement** is manufactured in Haiphon (French Indo-China) and together with **Coal and Zinc Ore** formed the principal mineral exports. (P. 902.)

The principal **Essential Oils** exported from Hongkong to the U. S. and Europe are aniseed, cassia, and peppermint. (P. 906.)

## BOOK REVIEWS

**Molded Electrical Insulation and Plastics.** By EMILE HEMMING. New York: Ward Clausen Co. 207 pages. Illustrated. Price, \$3.00.

This a new book in the very meaning of the word since no treatise on that subject has heretofore appeared. The author by saying in the introduction—"a series of new inventions in the field of electrical insulation products have been developed and enormous progress has been made"—is fully justified, since practically a new industry has grown up in the manufacture of plastics and insulating materials, due to the remarkable progress made in the electrotechnical art and not the least due to the rapid development of chemistry also in this field within the last decade.

The reader, passing over in the book the very striking definition of molded insulation and the history of its development within the last ten years, finds himself transferred "in medias res," the curtain is raised and there is presented to the spectators' eyes a very intuitive and original classification of molded insulation products and plastics. How important a part in the manufacture of these compounds plays the proper selection of the raw materials is shown in the chapter, "Raw Materials," which surely will be of special interest to the chemist.

Articles like "Hydraulic Cement," "Shellac," "Formaldehyde," "Phenol," "Condensation," may be especially marked.

In the following chapters, dealing with the different classes of molded materials and describing the hot and cold molding processes, there are very instructive essays, e. g., "Ceramics," "Rubber Compounds," "Organic Plastics" (Celluloid Albuminoids) and "Synthetic Resinous Materials." The author gives a clear and full discussion of the properties of the molded materials as to life, puncture tests, mechanical strength, weather and heat-proof qualities, resistance to chemical action, etc., which shows the intimate knowledge and broad experience of the worker.

A feature of the book is the many illustrations of molded articles from properly composed plastic materials. The author shows how, by chemical synthesis, plastics have recently been produced, which have superseded a great many of the older insulating materials.

The chemist, chemical student, engineer and manufacturer will find in this book what has been done in the manufacture of plastics and insulating products and what is to be done yet to improve the qualities of these materials in order to fulfill the conditions necessary to produce a perfect insulator.

W. SANGER

**Die Chemie und Technologie der Natürlichen und Künstlichen Asphalte.** DR. HIPPOLYT KÖHLER. Zweite Vollständig Umgearbeitete und Stark Vermehrte Auflage Herausgegeben von Dr. Hippolyt Köhler, Direktor der Rutgerswerke-Aktiengesellschaft, Berlin, und Dr. Edmund Graefe, Direktor der Duetschen Trinidad-Asphalt-Gesellschaft m.b.H., Dresden. 504+xxi pages. Braunschweig, Verlag von Friedr. Vieweg & Sohn, 1913. Paper, \$4.50.

This publication forms the 7th part of the "Neues Handbuch der Chemischen Technologie" which is being issued under the editorship of Dr. C. Engler. The first edition, by Köhler alone, appeared in 1904 and was a noteworthy compilation at that time. In associating with himself Dr. Edmund Graefe, Dr. Köhler has been enabled to bring the subject in essential particulars

up to date in a most satisfactory manner, especially as regards the uses of the native bitumens in the United States in the construction of pavements and roads, owing to Dr. Graefe's connection with the industry in this country and his intimate acquaintance with the processes which are being employed.

The contents of the book are divided into three parts: *First*, an historical consideration of the materials under consideration, the occurrence of the natural asphalts as known at the present time, the origin of bitumen and of asphalt, the physical and chemical properties, composition and components of asphalts, and finally, a chapter on "Artificial Asphalts" prepared from coal-gas tar, brown coal tar and from petroleum, as well as reference to oil-gas tar, water-gas tar, montan pitch, the pitches obtained in the saponification of the fats and resin pitches.

*The Second*, or technical part, is descriptive of the industries in which asphaltic materials are used, structurally for pavements, roads and water-proofing, and industrially in the preparation of roofing felts and water-proofing papers, as well as for insulating material. Attention is also called to the uses of asphalt in rubber substitutes, in varnishes and cementing materials, in the formation of tubes, cork asphalt, as an insulating material and in photographic processes.

*The Third*, or analytical part, summarizes very thoroughly the physical and chemical methods in use in the investigation of the natural and so-called artificial asphalts, and the technical testing and examination of asphaltic materials of all descriptions.

The book is a compilation of the results of practically everything that has been done in all parts of the world, in the study of the solid native bitumens and their surrogates, both as to their occurrence, nature and origin, and their applications in all of the industries. The data have been assembled with that thoroughness and detail which is characteristic of books of this type which are published in Germany. It can be criticized only because it is too thorough in this respect, and includes much material which the exercise of good judgment might have eliminated as being of doubtful value. Looked at from any point of view, the book is a monumental one, and will be found of the greatest value in the hands of any one who can make use of the German language, and it can be highly recommended to all who are interested in the subject of which it treats. The new edition contains 504 pages as compared with the 433 of the first edition.

CLIFFORD RICHARDSON

**Solvent Oils, Gums, Waxes and Allied Substances.** F. H. HYDE. D. Van Nostrand Company, New York. \$2.00.

This book is a very short compilation of the chemical and physical properties of the above substances. It includes some of the more common methods of analysis and tests for oils and fats and concludes with chapters on alkaloidal substances, bitter principles and various miscellaneous substances.

Such a conglomeration condensed to 170 small pages must necessarily be of very limited value.

The chapter on proteins which the author labels "Albumenoids or Proteids" is particularly antiquated.

SIDNEY BORN

**Practical Science for Engineering Students.** By H. STANLEY. Published by Methuen and Company, Ltd., 36 Essex Street, Strand, W. C., London. Price, \$0.75.

This book was written, according to the author, "primarily

to suit the needs of evening students who have passed the very elementary stages. It should also be useful, it is hoped, to those entering on an engineering training proper, who have not gone through a good course of laboratory work."

In the opinion of the reviewer, while the book contains some

good information, the treatment, though clear, is so superficial that it is likely to mislead the beginner for whom it is primarily written. The tables of constants do not, in many cases, contain the latest values.

G. V. WENDELL

## NEW PUBLICATIONS

By D. D. BEROLZHEIMER, Librarian The Chemists' Club, New York

**Carbohydrates, Short Handbook of the.** By B. TOLLENS. 3rd Ed. 8vo. 816 pp. Price, \$5.50. J. A. Barth, Leipzig. (German.)

**Catalysts, The Biochemical, in Life and in Industry.** By JEAN EFFRONT. 8vo. 772 pp. Price, \$5.00. Dunod & Pinat, Paris. (French.)

**Chemistry and Its Borderland.** By ALFRED W. STEWART. 8vo. Price, \$1.25. Longmans, Green & Co., New York.

**Chemistry, General, Physical and Theoretical, Textbook of.** Vol. I. By W. KUESTER and A. THIEL. 2 Vols. L. 8vo. Price, \$4.75. Carl Winter, Heidelberg. (German.)

**Chemistry, Scientific, Progress of, in Our Own Times.** By WILLIAM A. TILDEN. 2nd Ed. 8vo. 366 pp. Price, \$2.25. Longmans, Green & Co., New York.

**Cotton, Its Origin, Use, History and Significance.** By KARL STEUCK-ART. 8vo. 59 pp. Price, \$1.00. Bernhard F. Voigt, Leipzig. (German.)

**Engineering, Chemical, Notes on.** By J. W. HINCHLEY. 8vo. J. & A. Churchill, London

**Factory Organization and Administration.** By HUGO DIEMER. 8vo. 370 pp. Price, \$3.00. McGraw-Hill Book Co., New York.

**Fibers, Spinning Animal and Mineral.** By D. DE PRAT. 8vo. 482 pp. Price, \$1.75. L. Mulo, Paris. (French.)

**Fuel, Solid, Liquid and Gaseous.** By J. S. S. BRAME. 8vo. 372 pp. Price, \$3.25. Edward Arnold, London.

**Metal Coloration and its Production.** By G. BUCHNER. 5th Ed. Lex. 8vo. 426 pp. Price, \$2.25. M. Krayn, Berlin. (German.)

**Metallic, Inter-, Compounds.** By C. H. DESCH. 8vo. 116 pp. Price, \$0.75. Longmans, Green & Co., New York.

**Organic Compounds, Chemical, Technology of.** By R. O. HERZOG. 8vo. 732 pp. Price, \$5.50. Carl Winter, Heidelberg. (German.)

**Physics, Molecular.** By J. A. CROWTHER. 8vo. J. & A. Churchill, London.

**Plastics, Molded Electrical Insulation and.** By EMILE HEMMING. 8vo. Price, \$3.00. Ward Clausen Co., New York.

**Refrigeration, Mechanical.** By H. J. MACINTYRE. 8vo. 346 pp. Price, \$4.25. Chapman & Hall, London.

**Silk, Raw.** By L. DURAN. Cr. 8vo. Price, \$2.75. Spon & Co., London.

**Sugar Industry, Chemistry of the.** By OSKAR WOHRZYER. 8vo. 160 pp. Price, \$5.00. Julius Springer, Berlin. (German.)

**Tanning Laboratories, Chemical, Handbook for.** By GEORG GRASSER. L. 8vo. 400 pp. Price, \$3.75. Schulze & Co., Leipzig. (German.)

**Viscosity of Liquids.** By A. E. DUNSTAN and F. B. THOLE. 8vo. 92 pp. Price, \$0.90. Longmans, Green & Co., New York.

**Water Purification, Modern Methods of.** By J. DON and J. CHISHOLM. 8vo. 398 pp. Price, \$4.20. Longmans, Green & Co., New York.

### RECENT JOURNAL ARTICLES

**Acids, Mineral, Report on the, Industry in 1913.** By K. REUSCH. *Chemiker Zeitung*, Vol. 38, 1914, No. 36, pp. 383-386.

**Alloys, Non-Ferrous, Nomenclature of.** ANONYMOUS. *Industrial Engineering*, Vol. 14, 1914, No. 2, pp. 69-71.

**Ammonia Condenser, The.** By A. G. SOLOMON. *Practical Engineer*, Vol. 18, 1914, No. 6, pp. 353-359.

**Ammonia, Electrochemical, Oxidation of.** By G. OESTERHELD. *Zeitschrift fuer anorganische Chemie*, Vol. 86, 1914, No. 2, pp. 105-142.

**Ammonia, Synthetic, by the Serpek Process.** By HERRE. *Chemiker Zeitung*, Vol. 38, 1914, No. 29, pp. 317-318.

**Blast Furnace, Use of Dry Air in.** By H. G. GIRVIN. *Journal of the Society of Chemical Industry*, Vol. 33, 1914, No. 6, pp. 283-284.

**Brandy, Manufacture, Properties and Uses of.** By A. I. PEROLD. *Agricultural Journal of the Union of South Africa*, Vol. 7, 1914, No. 2, pp. 180-192.

**Cellulose and Sulfité, Copper-figure and True-acid-figure of.** By ERICH RICHTER. *Pulp and Paper Magazine of Canada*, Vol. 12, 1914, No. 7, pp. 193-197.

**Coal, Combustion of, and Smoke Abatement.** By SAMUEL B. FLAGG. *Industrial World*, Vol. 48, 1914, No. 13, pp. 368-372.

**Coal Gas, Notes on Naphthalene in.** By JAMES MACLEOD and JAS. H. R. HENDERSON. *Journal of the Society of Chemical Industry*, Vol. 33, 1914, No. 6, pp. 299-301.

**Coke, By-product, The Manufacture of.** By T. V. SALT. *Chemical Engineer*, Vol. 19, 1914, No. 3, pp. 91-103.

**Condensing (Cooling) Apparatus, Counter-current, The History of the.** By MAX SPETER. *Chemische Apparatus*, Vol. 1, 1914, No. 5, pp. 65-70.

**Copper Ores, Hydro-Electrolytic Treatment of.** By ROBERT R. GOODRICE. *Reprint. Transactions American Electrochemical Society*, Vol. 25, 1914, No. 22, pp. 1-36.

**Copper Tailings, Leaching of.** By RUDOLF GAHL. *Reprint. Transactions American Electrochemical Society*, Vol. 25, 1914, No. 19, pp. 1-9.

**Cyanamid, Polymerization of.** By GEORGE F. MORRELL and PETER BUREN. *Journal of the Chemical Society*, Vols. 105-106, 1914, No. 617, pp. 576-589.

**Cyanids, Speed of Hydrolysis in Hydrochloric Acid Solution.** By SOLO KILPI. *Zeitschrift fuer physikalische Chemie*, Vol. 86, 1914, No. 6, pp. 641-681.

**Denitrification, The Mechanism of.** By WILLIAM HULME. *Journal of the Chemical Society*, Vols. 105-106, 1914, No. 617, pp. 623-632.

**Electrochemical Industries, The Present State of the.** By HENRY GALL. *Revue générale de chimie pure et appliquée*, Vol. 17, 1914, No. 2, pp. 21-30.

**Heat Insulators.** By JEAN ROUSSET. *Revue générale de chimie pure et appliquée*, Vol. 17, 1914, Nos. 2 and 3, pp. 31-37, 41-52.

**Hydrogenation: Catalytic Reduction of Unsaturated Fatty Acids by Means of Nickel and Nickel Oxid.** By W. MERGIN and G. BARTELS. *Journal fuer praktische Chemie*, Vol. 89, 1914, Nos. 5 & 7, pp. 290-301.

**Indigo, New Derivatives of, and of Other Indigoid Dyestuffs.** By G. ENGL. *Zeitschrift fuer angewandte Chemie*, Vol. 27/I, 1914, No. 20, pp. 144-148.

**Industrial Processes, Lenses for Protection of the Eyes in.** By M. LUCKIESH. *Industrial World*, Vol. 48, 1914, No. 15, pp. 431-432.

**Insulating Materials, The, of Electrotechnics and Their Examination.** By F. W. HINRICHSSEN. *Kunststoffe*, Vol. 4, 1914, Nos. 3 and 4, pp. 41-43 and 64-65.

**Iron, Electrolytic, Microscopic Study of.** By OLIVER W. STOREY. *Reprint. Transactions American Electrochemical Society*, Vol. 25, 1914, No. 15, pp. 1-39.

**Iron, Action of Concentrated Sulfuric Acid on.** By CHARLES E. FAWSITT and CHARLES W. R. POWELL. *Journal of the Society of Chemical Industry*, Vol. 33, 1914, No. 5, pp. 234-237.

**Metal, Type, The Cause of the Oxidation of the.** By RICHARD MEYER and SIEGFRIED SCHUSTER. *Zeitschrift fuer angewandte Chemie*, Vol. 27/I, 1914, No. 18, pp. 121-127.

**Metallurgy: Treatment of Cyanid Precipitate.** By HERBERT A. MCGRAW. *Engineering and Mining Journal*, Vol. 97, 1914, No. 10, pp. 505-509.

**Metallurgical Problems, Some Present-day.** By D. A. LYON. *Journal of the Franklin Institute*, Feb., 1914.

**Paints, Fire Retardant, for Shingles.** By HENRY A. GARDNER. *Drugs, Oils and Paints*, Vol. 29, 1914, No. 10, pp. 370-374.

**Paper: Chemical Pulp, Bleaching of, and Suggestions for a Standard Method.** By ARTHUR BAKER and JAMES JENNISON. *Journal of the Society of Chemical Industry*, Vol. 33, 1914, No. 6, pp. 284-288.

**Pipes, Wood-lined, Production and Utilization of.** By H. WINKELMANN. *Zeitschrift fuer angewandte Chemie*, Vol. 27/I, 1914, No. 24, pp. 182-183.

**Power and Heat Costs in Chemical Works.** By T. ROLAND WOLLASTON. *Journal of the Society of Chemical Industry*, Vol. 33, 1914, No. 6, pp. 293-298.

**Rubber, Field, Newer Work in the.** By A. HOLT. *Zeitschrift fuer angewandte Chemie*, Vol. 27/I, 1914, No. 22, pp. 153-158.

**Soap, The Testing of.** By K. B. LAMB. *Textile World Record*, Vol. 46, 1914, No. 6, pp. 83-86.

**Surface Tension and Surface Energy and Their Influence on Chemical Phenomena.** By R. S. WILSON and E. HATSCHER. *Chemical World*, Vol. 3, 1914, No. 4, pp. 112-114.

**Textils, Some Notes on Bleaching.** By CHEMICUS. *Cotton*, Vol. 78, 1914, No. 5, pp. 219-221.

**Wood Preservation with Water-Soluble Substances, The Future of.** By BASILIUS MALENEKOVIC. *Zeitschrift fuer angewandte Chemie*, Vol. 27/I, 1914, No. 18, pp. 132-135.

**Zinc, Electrodeposition of, at High Current Densities.** By JOHN N. PRING and ULRICH C. TAINTON. *Journal of the Chemical Society*, Vols. 105-106, 1914, No. 617, pp. 710-724.



# MARKET REPORT

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR THE MONTH OF APRIL, 1914

## ORGANIC CHEMICALS

Acetanilid.....	Lb.	21 1/2	@	2 1/2
Acetic Acid (28 per cent).....	C	1.50	@	1.65
Acetone (drums).....	Lb.	10 1/2	@	11
Alcohol, denatured (180 proof).....	Gal	35	@	37
Alcohol, grain (188 proof).....	Gal	2.52	@	2.54
Alcohol, wood (95 per cent).....	Gal	45	@	47
Amyl Acetate.....	Gal	1.60	@	1.65
Aniline Oil.....	Lb.	9 1/2	@	10
Benzoic Acid.....	Lb.	23	@	27
Benzol (90 per cent).....	Gal	23	to	25
Camphor (refined in bulk).....	Lb.	@		42 1/2
Carbolic Acid (drums).....	Lb.	7 1/4	@	8
Carbon Bisulfide.....	Lb.	6 1/2	@	8
Carbon Tetrachloride (drums).....	Lb.	7 1/4	@	7 1/2
Chloroform.....	Lb.	19	@	24
Citric Acid (domestic), crystals.....	Lb.	51	@	51 1/2
Dextrine (corn).....	C.	2.52	@	2.72
Dextrine (imported potato).....	Lb.	5 1/2	@	6 1/2
Ether (U. S. P., 1900).....	Lb.	18	@	24
Formaldehyde.....	Lb.	8 1/2	@	9 1/2
Glycerine (dynamite).....	Lb.	19 1/2	@	19 1/2
Oxalic Acid.....	Lb.	7 1/4	@	7 1/2
Pyrogallol Acid (bulk).....	Lb.	1.20	@	1.40
Salicylic Acid.....	Lb.	25	@	27
Starch (cassava).....	Lb.	3 1/4	@	4
Starch (corn).....	C.	1.84	@	2.50
Starch (potato).....	Lb.	5	@	5 1/2
Starch (rice).....	Lb.	7	@	8
Starch (sago).....	Lb.	2 1/2	@	2 1/2
Starch (wheat).....	Lb.	5 1/4	@	6 1/2
Tannic Acid (commercial).....	Lb.	35	—	36
Tartaric Acid, crystals.....	Lb.	@		30 1/4

## INORGANIC CHEMICALS

Acetate of Lead (brown, broken).....	Lb.	7 1/4	@	7 1/2
Acetate of Lime (gray).....	C.	1.50	@	1.55
Alum (lump).....	C.	1.75	@	2.00
Aluminum Sulfate (high-grade).....	C.	1.25	@	1.75
Ammonium Carbonate, domestic.....	Lb.	8	@	8 1/2
Ammonium Chloride, gray.....	Lb.	57 1/2	@	61 1/2
Aqua Ammonia (drums) 16°.....	Lb.	2 1/4	@	2 1/2
Arsenic, white.....	Lb.	3	@	3 1/2
Barium Chloride.....	C.	1.60	@	1.62 1/2
Barium Nitrate.....	Lb.	5	to	5 1/4
Barytes (prime white, foreign).....	Ton	19.00	@	23.50
Bleaching Powder (35 per cent).....	C.	1.20	@	1.30
Blue Vitriol.....	C.	4.80	@	5.00
Borax, crystals (bags).....	Lb.	3 1/4	@	4 1/2
Boric Acid, crystals (powd.).....	Lb.	7	@	8
Brimstone (crude, domestic).....	Ton	22.00	@	22.50
Bromine, bulk.....	Lb.	30	@	35
Calcium Chloride, fused.....	C.	57 1/2	@	65
Chalk (light precipitated).....	Lb.	4	@	4 1/4
China Clay (imported).....	Ton	nominal		
Feldspar.....	Ton	8.00	@	12.00
Fuller's Earth, powdered, Foreign.....	Ton	16.00	@	17.00
Green Vitriol (bulk).....	C.	55	@	60
Hydrochloric Acid (18°).....	C.	1.15	@	1.65
Iodine (resublimed).....	Lb.	3.55	@	3.60
Lead Nitrate.....	Lb.	8	@	8 1/2
Litharge (American).....	Lb.	5 1/2	@	5 1/4
Lithium Carbonate.....	Lb.	65	@	70
Magnesium Carbonate.....	Lb.	21	@	35
Magnesite "Calcined".....	Ton	28.50	@	29.50
Nitric Acid, 36°.....	Lb.	37 1/2	@	41 1/4
Phosphoric Acid (sp. gr. 1.75).....	Lb.	20	@	24
Phosphorus.....	Lb.	45	@	1.00
Plaster of Paris.....	Bbl.	1.50	@	1.70
Potassium Bichromate, 50°.....	Lb.	6 1/4	@	7
Potassium Bromide.....	Lb.	39	@	40
Potassium Carbonate (calcined), 80 @ 85%.....	C.	3 1/2	@	3 1/4
Potassium Chlorate, crystals.....	Lb.	7 1/4	@	7 1/4
Potassium Cyanide (bulk), 98-99%.....	Lb.	19	@	22
Potassium Hydroxide.....	C.	3.87 1/2	@	4.37 1/2
Potassium Iodide (bulk).....	Lb.	2.95	@	3.00
Potassium Nitrate (crude).....	Lb.	4 1/2	@	5 1/4
Potassium Permanganate (bulk).....	Lb.	4 1/2	@	10
Quicksilver, Flask (75 lbs.).....	37.50	@	—	
Red Lead (American).....	Lb.	6	@	6 1/4
Salt Cake (glass makers').....	C.	55	@	65

Silver Nitrate.....	Oz.	367 1/2	@	387 1/4
Soapstone in bags.....	Ton	10.00	@	12.00
Soda Ash (48 per cent).....	C.	67 1/2	@	72 1/2
Sodium Acetate.....	Lb.	3 1/4	@	4 1/8
Sodium Bicarbonate (domestic).....	C.	1.00	@	1.10
Sodium Bicarbonate (English).....	Lb.	2 1/4	@	3
Sodium Bichromate.....	Lb.	4 1/8	@	47 1/8
Sodium Carbonate (dry).....	C.	60	@	80
Sodium Chlorate.....	Lb.	7 1/4	@	7 1/2
Sodium Hydroxide, 60 per cent.....	C.	1.55	@	1.57 1/2
Sodium Hyposulfite.....	C.	1.30	@	1.60
Sodium Nitrate, 95 per cent, spot.....	C.	—	@	2.25
Sodium Silicate (liquid).....	C.	65	@	1.50
Strontium Nitrate.....	Lb.	6 3/4	@	7
Sulfur, Flowers (sublimed).....	C.	2.20	@	2.60
Sulfur, Roll.....	C.	1.85	@	2.15
Sulfuric Acid, 60° B.....	C.	85	@	1.00
Talc (American).....	Ton	15.00	@	20.00
Terra Alba (American), No. 1.....	C.	75	@	80
Tin Bichloride (50°).....	Lb.	11 1/4	@	12 1/2
Tin Oxide.....	Lb.	42	@	44
White Lead (American, dry).....	Lb.	5 1/4	@	5 1/2
Zinc Carbonate.....	Lb.	8 1/2	@	9
Zinc Chloride (granulated).....	Lb.	4 1/2	@	5
Zinc Oxide (American process).....	Lb.	5 1/8	@	6 1/4
Zinc Sulfate.....	Lb.	2 1/4	@	2 1/8

## OILS, WAXES, ETC.

Beeswax (pure white).....	Lb.	45	@	47
Black Mineral Oil, 29 gravity.....	Gal.	13 1/2	@	14
Castor Oil (No. 3).....	Lb.	8 1/4	@	8 1/2
Ceresin (yellow).....	Lb.	12	@	22
Corn Oil.....	C.	6.45	@	6.50
Cottonseed Oil (crude), f. o. b. mill.....	Gal.	47	@	47 1/2
Cottonseed Oil (p. s. y.).....	Lb.	7 3/8	@	7 1/8
Cylinder Oil (light, filtered).....	Gal	21 1/2	@	32
Japan Wax.....	Lb	12 1/2	@	13
Lard Oil (prime winter).....	Gal	93	@	95
Linsed Oil (raw).....	Gal	50	@	51
Menhaden Oil (crude).....	Gal	nominal		
Neatsfoot Oil (20°).....	Gal	96	@	98
Paraffine (crude, 120 & 122 m. p.).....	Lb.	3 1/2	@	3 1/4
Paraffine Oil (high viscosity).....	Gal.	27	@	28
Rosin ("F" grade) (280 lbs.).....	Bbl.	4 35	@	—
Rosin Oil (first run).....	Gal.	@		27
Shellac, T. N.....	Lb.	16	@	16 1/2
Spermaceti (cake).....	Lb.	30	@	31
Sperm Oil (bleached winter), 38°.....	Gal.	72	@	73
Spindle Oil, No. 200.....	Gal.	17 1/2	@	18 1/2
Stearic Acid (double-pressed).....	Lb.	8 1/4	@	11 1/4
Tallow (acidless).....	Gal	65	@	66
Tar Oil (distilled).....	Gal	30	@	31
Turpentine (spirits of).....	Gal.	47	@	47 1/4

## METALS

Aluminum (No. 1 ingots).....	Lb.	17 3/4	@	18 1/4
Antimony (Hallet's).....	Lb.	7	@	7 1/4
Bismuth (New York).....	Lb.	2.05	@	2.10
Bronze powder.....	Lb.	50	@	3.00
Copper (electrolytic).....	C.	14.30	@	14.37 1/2
Copper (lake).....	Lb.	14 1/8	@	14 1/2
Lead, N. Y.....	Lb.	3	@	—
Nickel.....	Lb.	50	@	55
Platinum (refined).....	Oz.	43.50	@	44.50
Silver.....	Oz.	58	@	58 1/4
Tin.....	C.	36.00	@	37.00
Zinc.....	C.	5.20	@	—

## FERTILIZER MATERIALS

Ammonium Sulfate.....	C.	2.75	@	2.80
Blood, dried.....	Unit	—	@	3.45
Bone, 4 1/4 & 50, ground, raw.....	Ton	29.00	@	30.00
Calcium Nitrate (Norwegian).....	C.	2.05	@	2.15
Castor meal.....	Unit	nominal		
Fish Scrap, domestic, dried.....	Unit	nominal		
Phosphate, acid, 16 per cent bulk.....	Ton	7.00	@	—
Phosphate rock, f. o. b. mine.....	Ton	—	@	—
Florida land pebble, 68 per cent.....	Ton	2.25	@	2.50
Tennessee, 70-80 per cent.....	Ton	5.00	@	5.50
Potassium, "muriate," basis 80 per cent.....	Ton	39.07	@	—
Pyrites, furnace size, imported.....	Unit	0.13 1/4	@	—
Tankage, high-grade.....	Unit	3.20	@	10

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## TABLE OF CONTENTS

EDITORIALS:		A Simple Extraction Apparatus. By Percy H. Walker and Lorin H. Bailey.....	497
Recent Synthetic Studies in the Tannin Group.....	450		
ORIGINAL PAPERS:		ADDRESSES:	
A Thermoelectric Method for the Determination of the Purity of Platinum Ware. By George K. Burgess and P. D. Sale.....	452	Recent Improvements in Gas Manufacture. By Alfred E. Forstall.....	499
The Determination of the Dust Fall in the Neighborhood of Cement Plants. By J. P. Mitchell.....	454	Chemistry an Important Factor in the Fertilizer Industry. By J. E. Breckeuridge.....	505
The Combustion Method for the Direct Determination of Rubber. By L. G. Wesson.....	459	OBITUARIES:	
Osage Orange—Its Value as a Commercial Dyestuff. By F. W. Kressmann.....	462	Herman Frasch, 505; Paul L. V. Hérault.....	506
The Reserve Supply of Phosphate Rock in the United States. By W. H. Waggaman.....	464	CURRENT INDUSTRIAL NEWS: A New Type of Artificial Fertilizer; A New Coal Calorimeter; Electric Smelting of Iron at Hardanger, Norway; The Fluxograph Flow Recorder; Industrial Accidents in Massachusetts; Vacuum Tar; Requirements of Glass for Bottling Medicine; Method of Scurfing Gas Retorts; Industrial Conditions in France; Electric Testing Bureaus in Germany; Steam Raising by Gas Coke; A Mercury Engine; A European View of the Monroe Doctrine; Enforcement of So-Called Net Weight Law; Russian Trade in Fertilizers in 1913; Natural Gas in Hungary.....	507
Determination of Carbon in Steel and Iron by the Barium Carbonate Titration Method. By J. R. Cain.....	465	SCIENTIFIC SOCIETIES:	
The Determination of Ammonia in Illuminating Gas. By J. D. Edwards.....	468	Report of Progress by Committee on Quality of Platinum Laboratory Utensils, April 9, 1914.....	512
The Study of the Crude Petroleum from Bioritsu, Formosa. By Tetsu. Katayama.....	469	Fertilizer Chemistry Division Report.....	513
Thermal Reactions in Carbureting Water Gas. Part II—Experimental. By M. C. Whitaker and W. F. Rittman.....	472	Report of the Analytical Committee—Rubber Section Comments of Joint Rubber Insulation Committee on Report of Analytical Committee of Rubber Section American Institute of Chemical Engineers, 6th Semi-Annual Meeting, Troy, June 17-20, 1914.....	515
Note on a Black Band Iron Ore from the Stearns Company's Coal Mines and on the Calcium-Magnesium Ratio in Kentucky Carbonate Ores. By Alfred M. Peter.....	479	NOTES AND CORRESPONDENCE:	
A Note on the Utilization of Muds and Scums from Sugar Refineries. By R. F. Gardiner.....	480	Formula for Contents of Cylindrical Tanks with Spherical Ends.....	517
The Effect of High Temperature on Yeast. By C. B. Cochran and J. H. Perkins.....	480	Influence of Rate of Stirring on Titre of Fats..	517
Physical Factors which Influence the Percentage of Wet and Dry Gluten in Wheat Flour. By B. H. Kepner.....	481	A Shaker for the Mechanical Analysis of Soils.....	517
The Determination of the Acetyl Number of Oils, Fats, Etc. By Edward B. Holland.....	482	Benzoic Acid in Prunes and Cranberries.....	518
A Comparison of Neutral Ammonium Citrate with Sodium Citrate and N/10 Citric Acid. By Paul Rudnick, W. B. Derby and W. L. Latshaw.....	486	Bureau of Standards' Analyzed Samples.....	518
The Effect of Ensilage Fermentation and Animal Digestion on the Solubility of Phosphoric Acid in Phosphate Rock. By C. A. Mooers.....	487	Platinum Thefts.....	518
The Theoretical Basis for the Commercial Preparation of Lime-Sulfur Spray. By Herman V. Tartar.....	488	PERSONAL NOTES.....	518
The Determination of Camphor in Tablets and Pills. By Edwin Doward.....	489	GOVERNMENT PUBLICATIONS.....	520
LABORATORY AND PLANT:		BOOK REVIEWS: Allen's Commercial Organic Analysis; The Electric Furnace; Principles and Practice of Agricultural Analysis; Metallography; Sugar Analysis; Industrial Poisoning; The Nickel Industry; with Special Reference to the Sudbury Region, Ontario.....	524
The Status and Tendency of the Gas Industry. By Walter R. Addicks.....	490	NEW PUBLICATIONS.....	527
		RECENT INVENTIONS.....	528
		MARKET REPORT.....	530

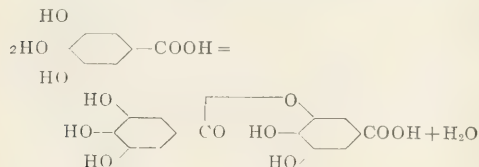
# EDITORIALS

## RECENT<sup>1</sup>SYNTHETIC STUDIES IN THE TANNIN GROUP<sup>1</sup>

There exist in nature a considerable number of substances whose aqueous extracts have the property of turning hide into leather. Substances which show this property have also certain other general characteristics. Tanning substances are amorphous and have an astringent taste. They usually precipitate gelatin from its solutions and form compounds with metals, those with iron, for example, being frequently colored and suitable for use as inks. Hydrolytic agents split them into a variety of products. One of these is almost always a sugar, usually *d*-glucose, while the other component is some hydroxy acid of the aromatic series. Caffetannic acid, for example, which is found in coffee and Paraguay tea, yields a sugar and caffeic acid. The tanning material of oak bark yields ellagic acid and quercite. Still others yield phloroglucinol<sup>1</sup> instead of sugar.

The most thoroughly studied of these substances is ordinary *tannin*, which occurs in the nut-galls of the oak and is also found in sumach, tea and other plants. It is a colorless, amorphous substance, which is readily soluble in water and only slightly soluble in alcohol and ether. It can be prepared in a state of comparative purity, and its structure has interested organic chemists for a long time.

The most important of the earlier investigations was carried on by Strecker in 1852 [*Ann. der Chemie*, **81** (1852), 248; **90** (1854), 328]. He hydrolyzed tannin and found three molecules of gallic acid associated with one of *d*-glucose. Many chemists who studied the problem later came to the conclusion that sugar was not an essential constituent, at least in all kinds of tannin, and the observation that gallic acid, by means of phosphorus oxychloride and other dehydrating agents, could be changed to digallic acid,



led Schiff, in 1871 [*Ber.*, **4** (1871), 232, 967; **12** (1879), 33; and *Ann.*, **170** (1873), 43], to accept this synthetic digallic acid as, at least, the principal component of tannin. Such a conclusion left the optical activity of tannin unexplained, since digallic acid contains no asymmetric carbon atom. It could not be certain, however, that optically active impurities might not be present, inasmuch as tannin is an amorphous substance and the usual criteria of purity and homogeneity in organic substances are lacking.

Walden, in 1897 [*Ber.*, **30** (1897), 3151; **31** (1898), 3167], made an extensive comparison of the synthetic

digallic acid with tannin, and found that their physical properties were not identical. The molecular weight of tannin is far too great for digallic acid, and neither the electrical conductivity, the absorption of light, nor the behavior with arsenic acid were found sufficiently parallel for Walden to believe in the identity of the substances concerned. Quite recently, Nierenstein made the suggestion that tannin might be a mixture of digallic acid with its optically active reduction product, leuco-tannin. Such a mixture, however, should be more acidic than tannin and have a smaller apparent molecular weight. Still more recently Feist [*Ber.*, **45** (1912), 1493] has suggested a more complex composition, but his conclusions have now been superseded by the work of Emil Fischer [*Gen. résumé, Ber.*, **46** (1913), 3253; see also **41** (1908), 2875; **45** (1912), 915, 2709, 3773; **46** (1913), 1116], which it is the principal object of this paper to describe.

Emil Fischer's attention was first devoted to the purification of tannin with the idea of obtaining as homogeneous a material as possible. For this purpose, the purest product from Chinese nut-galls was shaken from a dilute alkaline solution by ethyl acetate. It is obvious that a substance so purified could contain no free carboxyl group, and we can assume this to be the fact concerning the material investigated by Fischer. When purified in this way, the substance is amorphous, but it is doubtless as pure a tannin as has hitherto been prepared. It is optically active, the specific rotatory power being about 70°.

The next step was the hydrolysis of tannin. This was carried out in acid solution, since alkali would act upon any sugar formed. The method was checked by blank tests made with mixtures of gallic acid and sugar, and after making any necessary corrections of this kind, it was found that hydrolysis had decomposed the tannin into a mixture of one molecule of *d*-glucose and ten of gallic acid. No other hydroxy acid was found. Since there are five hydroxyl groups in *d*-glucose, a simple interpretation of the results would suggest that we had to do with an ester of glucose in which each of the five hydroxyl groups was esterified with a molecule of digallic acid. Such a substance would not be a glucoside in the ordinary acceptance of the term. Emil Fischer is of the opinion that the latter name should be reserved for products analogous in their structure to methyl glucoside,

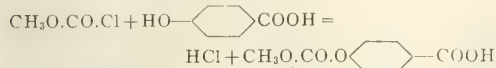


The best proof of the structure suggested for tannin would be its synthesis, but in view of the difficulty of preparing synthetic digallic acid, it seemed best to begin with the simpler problem of preparing glucose pentagalate. The method which first suggests itself for the preparation of such a compound is the treatment of the sugar by the chloride of the acid; but chlorides of substances like gallic acid are difficult to

<sup>1</sup> Address before the Eastern New York Section of the American Chemical Society, Schenectady, March 27, 1914.

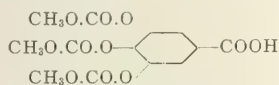


prepare. The usual easy reaction of the chlorides of phosphorus upon the free acids is complicated in this case by the fact that the hydroxyl groups also present are attacked by the reagent. Emil Fischer was able to avoid this difficulty by a method which he had previously used in less complicated cases. This consisted of treating a hydroxy acid with methyl chlorcarbonate. This forms a carbomethoxy derivative,

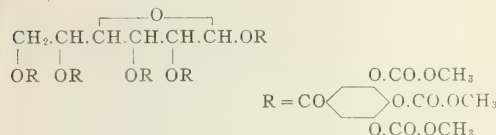


which is stable enough to tolerate reactions upon the carboxyl group, but when these reactions have been carried out, gentle hydrolytic agents exchange the carbomethoxy group for hydroxyl again.

It is obvious that under these circumstances gallic acid would yield a tricarbomethoxy derivative,

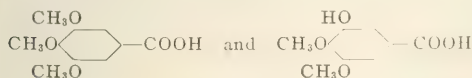


which, when treated with phosphorus chloride, would yield the corresponding acid chloride. This chloride was finally treated with *d*-glucose in dry chloroform solution, quinoline being introduced for the purpose of taking up the hydrochloric acid formed. The product was a penta-tricarbomethoxy-gallate of glucose,



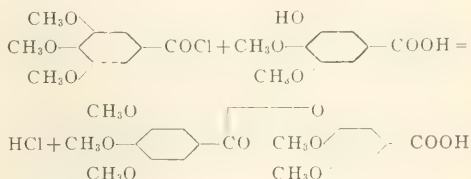
It was carefully saponified by means of a small excess of alkali dissolved in aqueous acetone. Under these circumstances the carbomethoxy groups were split off at ordinary temperature and the pentagallate of glucose was isolated. The similarity of this substance to ordinary tannin was striking. The only difference was in the rotatory power and the quantity of gallic acid formed by hydrolysis. Like tannin, the substance is amorphous, and it cannot be stated with certainty that it is perfectly homogeneous. Emil Fischer believes that there are probably at least two isomers present which stand to each other in the same relation as  $\alpha$ - and  $\beta$ -glucose. This condition of things is certain in the case of glucose pentabenzoate.

The next step was the preparation of methylotannin, which proved easier to carry out than the synthesis of tannin itself. Herzig [Ber., 38 (1905), 989; Monatshefte, 30 (1909), 543] had already prepared this substance by the action of diazomethane upon tannin, and had obtained, by hydrolysis, trimethylgallic acid and unsymmetrical *m,p*-dimethylgallic acid.



These facts suggest that tannin might be an ester

of glucose with five molecules of *m*-digallic acid. The synthesis was carried on much as before. Trimethylgalloyl chloride was first combined with *m,p*-dimethylgallic acid,



and this, in its turn, changed to its chloride and combined with *d*-glucose. The product was strikingly similar to that of Herzig, but there remains, of course, the same doubt as to its perfect homogeneity as in the other case.

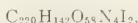
The success of these experiments seemed to warrant an attempt to prepare tannin itself: *m*-digallic acid, which had previously been synthesized, was changed to the carbomethoxy compound as in the simpler case of ordinary gallic acid, but the product was found to be amorphous, and the same is true of the chloride which is prepared from it. Finally, the combination with sugar took place only with difficulty and the synthesis cannot be regarded as successful. The essential nature of the tannins seems, however, to have been definitely settled by the investigation and we can be confident that the structure of tannin is typified by the penta-gallate of glucose. It is still possible, of course, that tannins from different sources have not exactly the same composition, and that any given sample of tannin is not homogeneous. It is also possible that the *d*-glucose is not readily formed in the molecule, but that there exists instead some polysaccharide which gives *d*-glucose upon hydrolysis.

The investigation was continued by combining gallic and other hydroxy acids with other sugars and polyatomic alcohols, and a variety of substances were thus prepared which showed the chief tannin characteristics. Doubtless the study of compounds of this class will be of considerable value to plant physiology since it is very likely that the plant builds up such substances as a means of neutralizing acids by esterification. Some practical results may also be expected, since small quantities of tannin-like substances have a marked influence upon the taste of such articles of food as tea, coffee and sweet fruits. It is, therefore, possible that synthetic materials of this type may find use as flavoring materials.

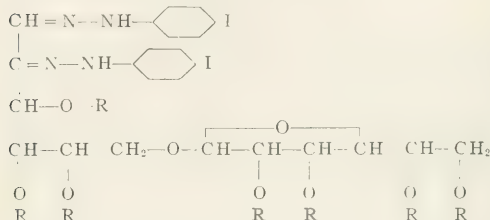
An interesting result of the investigation is to be found in the fact that syntheses of this kind lead naturally to products of extremely high molecular weight. In this property they surpass even the highest polypeptides. Emil Fischer expects to carry investigations of this sort further, believing that it is the duty of the Organic Chemist to build up as large molecules as possible, while the modern physicist is constantly dissecting the atom into smaller and smaller units.

By combining tribenzoylgallol chloride with the

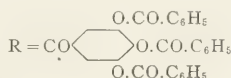
*p*-iodophenylosazone of maltose, Emil Fischer was able to prepare a substance of the formula



and molecular weight 4021. This substance has the highest molecular weight of any organic compound which has yet been prepared by synthesis. Its graphic formula is given below



and the only explanation necessary is that the radical R signifies tribenzoylgalloyl,



It is interesting to note that this substance follows the laws of Raoult very well. Determinations of the molecular weight by the freezing-point method, in bromoform, yielded numerical results which are surprisingly good when the magnitude of the molecule is taken into consideration.

This investigation has not led to the production of any substances which are sufficiently cheap to be of use to the tanner as a substitute for his extracts, but there has been brought upon the market within the last few months a laboratory product which is a promising substitute for tannin, and which is said by those in the trade to give good results and shorten the time required for tannage. This is the so-called "Neradol" of Stiasny [*Collegium*, 1913, p. 142]. It is prepared by treating phenol with sulfuric acid and adding formaldehyde in the proportion of one molecule of formaldehyde to two of phenol. This method of preparation suggests the well-known Bakelite, but the product differs from the latter in being soluble in water. It enters the pores of the hide readily, and when used as a preliminary treatment increases the velocity of tannage by other materials. It also produces leathers of good quality and light color.

F. J. MOORE

## ORIGINAL PAPERS

### A THERMOELECTRIC METHOD FOR THE DETERMINATION OF THE PURITY OF PLATINUM WARE<sup>1</sup>

By GEORGE K. BURGESS AND P. D. SALE

At the request of Dr. W. F. Hillebrand,<sup>2</sup> Chairman of the Committee on "Quality of Platinum Utensils," of the American Chemical Society, experiments on the loss in weight due to continued and repeated heating of platinum crucibles of varying degrees of purity have been undertaken, in continuation of similar experiments carried out under the immediate supervision of members of the above-mentioned committee.

From some of these earlier experiments, and from the work of other experimenters on the evaporation of metals of the platinum group, it appears to have been hoped to be able to classify platinum ware as to purity in terms of its evaporation at a definite temperature, say 1200° C. This seemed plausible in view of the fact that the usually predominant impurity, iridium, is very much more volatile than platinum. Even if this method, however, would give an indication of the platinum purity, which appears doubtful in the light of some of our more recent experiments, it is at best a somewhat tedious and delicate operation to carry out.

These experiments showed the desirability of having an accurate and rapid method for determining platinum purity and one that could be applied to crucibles without defacing them.

The most exact method for the determination of purity of platinum appears to be by measurement of its temperature coefficient of electrical resistance,

which quantity has a mean value of about 0.00391 per degree centigrade for the interval 0° to 100° C. for the purest obtainable platinum, and decreases with the addition of anything to the platinum. This measurement can be made conveniently and exactly only with wires and is therefore of little interest for the determination of the purity of platinum ware such as crucibles.

The thermoelectromotive force of platinum against many of its alloys has also been determined with considerable exactness.<sup>1</sup>

This property may evidently be made use of, therefore, in devising a method for the determination of platinum purity and one that possesses, furthermore, the advantages of accuracy, speed, convenience, and preservation intact of the objects tested.

The method as developed for use with crucibles is shown in Fig. 1. To the rim of the crucible *C* are arc-soldered, at *e* and *f*, two pure platinum wires of small diameter (0.1 or 0.2 mm.); these wires are connected to an ordinary pyrometer-galvanometer or millivoltmeter, *G*; the junction *e* is heated by a small oxy-gas or other blast flame from *d* and the junction *f* is kept cool by an air blast, *c*; a sheet of asbestos, *A*, cut as shown, serves to prevent radiation from the heated portion of the crucible reaching the cold junction *f*.

Temperatures are measured by means of a 90 Pt-10 Rh, Pt thermocouple using the cold junction as above and a Pt-Rh wire arc-soldered to the crucible near *c*, most conveniently adjacent to (0.5 to 1 mm. distant) but not touching the Pt wire at *e*.

<sup>1</sup> Presented at the 49th Meeting of the A. C. S., Cincinnati, April 6-10, 1914.

<sup>2</sup> See report of Platinum Committee in this issue.

<sup>1</sup> In particular: W. Geibel, *Z. anorg. Chem.*, **69** (1910), 38; **70** (1911), 240; Burgess and LeChatelier, "The Measurement of High Temperatures," 3rd Ed., 1913, p. 171.

The wires are attached at *e* and *f* by the well known arc-soldering method, which consists in making the

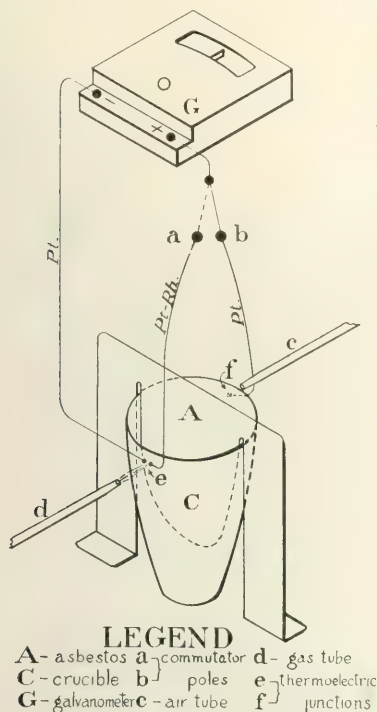


FIG. 1.—DETERMINATION OF PURITY OF PLATINUM WARE  
crucible one terminal of an electric circuit of about 40 volts and a sharpened graphite pencil the other, with a

crucible and at the same instant touching the wire to the crucible at this point. The end of the wire is thus fused to the crucible. With a little practice this operation may be made so that there is hardly any noticeable effect on the appearance of the crucible after the wire is removed.

Quite satisfactory results may also be obtained by simply touching the Pt wires to the crucible at *e* and *f*, or by clamping with platinum clips, without any soldering. With the apparatus once set up, a test may then be made in a few seconds and the crucible remains, of course, absolutely intact. The homogeneity of the crucible may also be determined by this method.

By means of a commutator at *a b*, measurements may be made alternately of the temperature at *e* and of the E. M. F. developed across the crucible when *e* is at this temperature. The commutator may also be designed so as to reverse *e* and *f* if it is desired to make *f* the hot junction.

It is, of course, essential that the two platinum wires be made of strictly pure platinum. For this purpose, use is made of Heraeus normal thermoelement wire drawn down; this platinum has shown itself to be a standard, uniform product, the purity of which is easily controlled by the electric resistance method above mentioned.

In the table are given the results of a series of measurements at about 1050° C. of the E. M. F. of pure platinum against "platinum" crucibles of various makes. In Fig. II are shown the isothermal curves, at 900°, 1000° and 1100° C., for iridium content of platinum in terms of E. M. F. against pure platinum. There is also shown here the iridium equivalent of the impurities in the crucibles *c*, *h* and *k* of the table, in terms of their stated and observed iridium contents.

It will be noted that all impurities are, for conve-

SUMMARY OF THERMOELECTRIC TESTS OF PLATINUM CRUCIBLES									
SOURCE OR MAKER	Stated Ir content Per cent	Previously heated Hrs.	Temp. of test °C.	Pt ss. crucible Mv.	E. M. F. Ir equivalent		E. M. F. from Pt-Ir curve (See 2 and 4) Mv.	E. M. F. excess due to Ir or impurities Mv.	Reference letter
					Pt ss. content Per cent	E. M. F. Ir equivalent			
Heraeus.....	0.0	17	1050	0.00	0.00	0.00	0.00	0.00	<i>a</i>
	0.7	Heated	1050	2.00	0.70	2.00	0.00	0.00	<i>b</i>
	0.7	0	1050	2.60	0.90	2.00	0.60	0.60	<i>c</i>
American Platinum Works.....	< 0.2	24	1050	0.63	0.19	0.10	0.53	0.53	<i>d</i>
	< 0.2	16	1050	1.00	0.35	0.10	0.90	0.90	<i>e</i>
	0.5 to 1.5	11	1075	6.60	2.55	1.50 to 4.10	2.50 to 5.10	4.90	<i>f</i>
	0.5 to 1.5	4	1085	6.40	2.30	1.50	4.90	3.50	<i>g</i>
	0.5	0.5	1100	3.50	1.19	...	3.50	3.50	<i>h</i>
Baker & Company.....	?	10	1050	6.75	2.72	...	6.75	6.75	<i>i</i>
	?	20	1050	6.95	2.78	...	6.95	6.95	<i>j</i>
	2.37	0	1030	6.00	2.37	6.00	0.00	0.00	<i>k</i>
	0.702	12	1050	1.90	0.66	2.05	-0.15	0.33	<i>l</i>
	Refined	0	1040	0.33	0.10	...	0.33	0.33	<i>m</i>
	?	3 yrs.	1100	3.00	1.01	...	3.00	3.00	<i>n</i>
	?	?	1100	1.71	0.55	...	1.71	1.71	<i>o</i>
Johnston Mathey & Company.....	?	67	1050	0.48	0.15	...	0.48	0.48	<i>p</i>
	?	0	1070	0.68	0.23	...	0.68	0.68	<i>q</i>
	?	20	1050	0.63	0.22	...	0.63	0.63	<i>r</i>
J. Bishop.....	?	9 mo.	1100	2.10	0.68	...	2.10	2.10	<i>s</i>
	?	0.5	1100	2.20	0.72	...	2.20	2.20	<i>t</i>
	Refined	31	1050	0.60	0.21	...	0.60	0.60	<i>u</i>
Quennessen De Belmont, Legendre et Cie.....	?	10	1050	2.79	0.98	...	2.79	2.79	<i>v</i>
	?	0	1060	2.80	0.98	...	2.80	2.80	<i>w</i>
	?	4	1030	1.60	0.56	...	1.60	1.60	<i>x</i>

rheostat in series. The operation of soldering consists in drawing a minute arc between pencil and

nience, expressed in terms of iridium content. Of particular interest is the comparison of columns 2 and 6,



the former giving the stated iridium content (and often accompanied by the statement that there are no other impurities) and the latter giving the iridium content as determined thermoelectrically by experiment and use of Fig. II. In several instances, notably for the

certain check on the platinum purity.<sup>1</sup> One of the most undesirable impurities often found in commercial platinum ware is iron; this is readily detected by ignition and subsequent washing with hot HCl and applying the usual color test for Fe. Iron, if present in

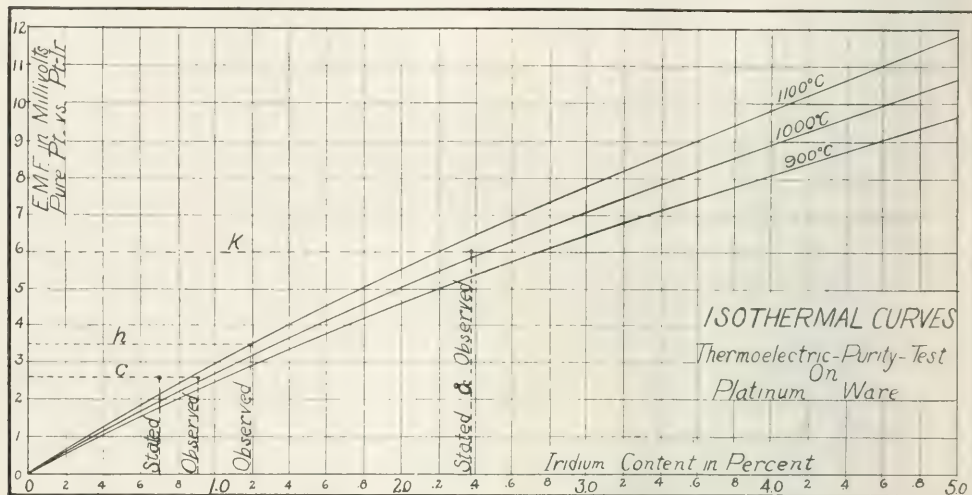


FIG. II.—IRIDIUM CONTENT VS. E. M. F. AGAINST PLATINUM

crucible of normal thermoelement platinum (a), of Heraeus and for Baker's crucible (k), of 2.37 per cent iridium, the stated and found iridium contents agree exactly. On the other hand there is a wide divergence from the supposed and actual iridium content for several of the crucibles; for example, f of the American Platinum Works, supposed to contain not over 0.50 to 1.5 per cent iridium, actually contains an iridium equivalent of 2.50 per cent; and even in the case of refined, specially refined and best crucible ware, the equivalent iridium content is not inconsiderable. Among the 22 crucibles examined there is but one, (i), of Baker & Co., containing less iridium than is stated.

In comparing the stated contents, column 2 of the table, it should be borne in mind that some of these crucibles, excepting perhaps those marked refined or specially refined, may contain iridium which is put or left in the crucible material purposely, usually for the purpose of stiffening, or in the case of commercial ware, because such Pt always carries Ir. The method here described, however, provides a delicate means of determining whether or not the desired limitation of impurity, expressed in terms of iridium content, and as measured thermoelectrically, has been met by the manufacturer. For the experimental arrangement here given, the amount of impurity is readily determined to 0.01 per cent and this accuracy could be improved upon if necessary.

The method does not distinguish the various possible impurities from each other but is nevertheless a

relatively considerable quantity, will also discolor the crucible on ignition.

It would probably be advantageous to substitute rhodium for iridium in platinum crucibles when stiffness is desired and when exact weighings have to be taken before and after ignition, for the reason that rhodium is far less volatile than iridium, and somewhat less so than platinum, although it appears not yet to have been proven that the more volatile metals alloyed in small amounts with platinum retain their volatility independently of the presence of the platinum.

The above described thermoelectric method will not alone distinguish between small amounts of rhodium and iridium, but a combination of the thermoelectric and loss of weight methods might be devised that would be satisfactory. An electric discharge method operated at high temperatures might possibly be made sufficiently selective to differentiate between platinum alloys of iridium and rhodium. There is evidently room for much more work along these lines.

BUREAU OF STANDARDS  
WASHINGTON

#### THE DETERMINATION OF THE DUST FALL IN THE NEIGHBORHOOD OF CEMENT PLANTS

By J. P. MITCHELL  
Received March 18, 1914

The determination of the dust fall in the neighborhood of cement plants, when alloyed with platinum (up to 90 per cent only of palladium) give, at high temperatures, an E. M. F. of the same sign against pure platinum. Therefore, there is no ambiguity in balancing one impurity against another.

hood of cement plants has recently become a matter of considerable importance, largely as a result of litigation which has arisen between certain companies engaged in the manufacture of cement, and the residents of the region in the immediate neighborhood of the plants. This litigation has taken the form of suits on the part of the residents either to secure damages, or obtain injunctions against the operation of the plants, based upon injury alleged to have been inflicted upon the property of the residents. Two entirely distinct claims of injury have been advanced. One is based upon the alleged infliction of actual damage to vegetation, either the actual destruction of plants and actual destruction, in whole or in part, of crops, or the lessening of the market value of plants and crops by the presence of cement dust on the plant foliage and fruit. The other claim is based upon the less specific ground of "nuisance." It is alleged that the cement dust enters the houses of the complainants, causes much personal inconvenience, and in general interferes with the right of every land holder to the enjoyment of normal and unpolluted atmospheric conditions. Whatever be the basis of the complaint, it is a matter of record that such complaints are becoming more common in all parts of the country, and in every such case it becomes a matter of importance to both parties that the true conditions be determined as accurately as possible. Such a determination involves a study of the amount and character of the dust fall throughout the region in question, and a correlation of the results of such a study with the prevailing meteorological conditions. It is the purpose of this paper to deal with the methods available for the determination of the dust fall, and the proper interpretations of the results obtained.

Another aspect of the subject deserves mention. From the cement manufacturer's point of view the dust thrown from the stacks of the plant represents not only a constant source of possible legal expense and anxiety, but also a very real economic waste. The amount of dust lost from a kiln of the ordinary rotary type may amount to a number of tons in one day, and this dust is not composed of a useless waste product, but is the very substance for the production of which the whole plant is operated. The recovery of this dust, therefore, should not be regarded entirely as an expense, but as a possible measure of economy. The determination of the amount of dust lost in this way from a given plant cannot be carried out satisfactorily by the determination of the dust fall in the vicinity, but must be arrived at by a study of the conditions existing in the stacks of the plant themselves, and therefore lies outside the scope of this paper.

The methods which have been used for the determination of the amount of dust in the atmosphere may be divided into four groups.<sup>1</sup>

The most scientifically accurate method is without doubt that of Aitkin. This depends upon condensing

water vapor on the dust particles, and counting the resulting drops of water.

This method is too refined for the purpose under consideration. The present problem is not concerned with the ultramicroscopical particles normally present in air, or even with the increase in their number, but rather with the very much larger particles of solid matter which constitute "dust" in the ordinary meaning of the term.

Efforts have been made to catch the dust present in air in various box-like contrivances designed to catch the dust by checking the velocity of the air currents, and create conditions under which the dust will settle out and remain within the apparatus. Such methods may be useful in a study of the character of atmospheric dust, but give rise to certain difficulties when applied to the problem of determining the amount of dust fall in different localities. Since the amount of dust remaining in the box depends upon the amount of air passing into it, that is, upon the wind velocity, the results give what may be termed the "dust burden" of the air, as distinguished from the "dust fall" which would have taken place at the same point had the velocity of the air not been checked.

The dust present in the air has been determined by drawing known volumes of air through water or filters, and weighing or counting the dust particles retained. This method again gives the "dust burden" of the air, rather than the "dust fall," and while it is available for determining the amount of dust in a given volume of air at a given time, it is not available for determining the relative dust fall at different points during a somewhat extended interval of time.

The fourth group of methods depends upon the exposure, in a horizontal position, of a surface of known area coated with a substance that will retain dust falling upon it, and the subsequent removal, weighing and examination of the dust deposited upon the surface. While no method of this sort collects the small microscopic particles present in large numbers in all air, it does collect the larger particles ordinarily considered "dust," and does afford a reliable means of comparing the amount and composition of the dust actually falling upon a horizontal surface at different points during a given interval of time. It is therefore available for the purpose here in view.

The method finally adopted as most efficient and practical is the exposure of glass plates coated with vaseline, and the subsequent cleaning of the plates with gasoline, and recovery of the dust by filtration. The details follow.

The plates used were of glass and measured five by seven inches. Ordinary window glass was used, and the dimensions of the plates were carefully checked, and any plates with variations greater than one-sixteenth of an inch were discarded. Old photographic plates may be used, but are thinner and more subject to breakage than ordinary window glass. Their lighter weight also makes them more difficult to handle in the field in a high wind. These plates were laid on horizontal platforms placed at the top of high poles. The size of the platforms was such

<sup>1</sup> For a very complete discussion of the methods available, and bibliography of the subject, see U. S. Dept. of Agriculture, Bureau of Soils, *Bull. No. 68*, "The Movement of Soil Material by the Wind," by E. E. Free.

that they just held the number of plates exposed, and projected less than half an inch beyond the outer edge of the outside plates. A wide projection, which could serve as a resting place for dust which might subsequently be blown onto the plates, was avoided. The plates were held in position by small tacks driven into the edge of the platform. The plates must be set closely together, and the tacks adjusted so as to hold the plates firmly in place, otherwise the shaking of the pole in a high wind will dislodge some of the plates. At the outset of the work some plates were lost from the platforms during a high wind storm, but with practice it was found that care in the adjustment of the tacks would prevent any loss from this cause. After the plates had been exposed for the desired length of time they were taken up, placed in tight wooden boxes provided with cleats to hold the plates apart, lowered to the ground, the box placed in a sack to exclude road dust, and taken to the laboratory.

The laboratory work involved the preparation and cleaning of the plates, and the weighing and analysis of the dust collected. Before use the plates were first thoroughly cleaned, then warmed, and while warm given a thin even coating of the purest vaseline obtainable (Kahlbaum). The vaseline while warm and liquid was best applied with a wide camel's hair brush. It was free from mineral salts, and gave no weighable residue when ignited. After exposure the plates were first carefully wiped on the edges and bottoms, and then placed in a white enamel photographic tray, and covered with filtered gasoline. The dust deposit was then loosened by rubbing with a camel's hair brush, the plates held on edge in the tray, and rinsed on both sides with a fine stream of gasoline blown from a wash bottle. All of one set of plates, which had been exposed on the same platform for the same time, were cleaned in the same tray of gasoline. Examination of the plates after the adhering gasoline had evaporated often disclosed fine streaks which looked like unremoved dust particles, but these streaks were found to be both volatile and soluble in alcohol, showing that all the mineral particles had been removed from the plates by the cleaning process.

The dust obtained in the trays was separated from the gasoline by filtration through paper filters. Some difficulty was experienced due to the hardening of the paper by the gasoline and consequent slow filtration. This difficulty can be overcome by first wetting the filter paper with alcohol, and by the use of moderately strong suction. The filtrates are never perfectly clear, but are slightly cloudy as a result, apparently, of the formation of an emulsion by the gasoline with some constituent of the vaseline. The evaporation of the filtrates in a number of cases, gave, after ignition, no weighable residue. The filter paper containing the dust was placed in a weighed platinum crucible, and heated cautiously to incipient redness until the paper was reduced to ash and the crucible and contents had attained constant weight. The result was corrected for the known weight of the filter paper ash.

The analysis of the dust samples was carried out according to standard methods. The sample was fused with sodium carbonate, digested with concentrated hydrochloric acid, and the silica determined after two evaporations and dehydrations, and was checked with hydrofluoric acid. The calcium was precipitated as calcium oxalate, after removal of iron and aluminum, from the boiling solution, and was ignited to calcium oxide until constant weight was obtained.

The choice of the locations for the exposure of the plates, the height of the platforms above the ground, the number of plates exposed in one set, and the length of time of the exposure involves the consideration of a number of factors. These factors all depend to some extent on the particular problem under investigation. Thus the topography of the country, the character of the vegetation, the climatic conditions, the season of the year, and the direction and regularity of the wind currents must all be considered, and none are identical in two specific problems. However, there are certain general principles that will apply to all cases.

Field work of this character is absolutely dependent upon fair weather. Even a light rain will interfere with the film of vaseline and adhering dust on the plates, causing "blisters" and bare spots to appear, and a heavy rain will not only wash the dust from the plates, but will also prevent the normal transportation of the dust from the plant by washing it out of the atmosphere before it has been carried to any distance. A period of settled fair weather must therefore be selected. This is vital, not only on account of the interference due to rain, but also on account of the importance of having normal wind conditions during the time of the investigation. In general, the spring and summer months are the most satisfactory; the winter months, when the wind currents are more variable, are far less desirable.

The locations selected for the exposure of the plates depend almost entirely on the objects of a particular investigation. If a lawsuit is involved, that will dictate at least some of the locations. In general, the positions selected should be at some distance from roads and buildings, and should be on exposed ground not sheltered by trees or hills. If a comprehensive study of the dust fall is under way they should be chosen in all directions from the plant, and at least one should be placed in a region clearly outside of the "dust zone" to serve as a control station.

The platforms are best placed on the top of poles from twenty-five to thirty feet above the ground. This height is important for two reasons: *First*, to place the plates above the influence of minor disturbances of the soil whether caused by man or wind. *Second*, to place the plates at an elevation where the wind currents are regular and approach, in velocity, those of the upper air currents. While nothing definite is known as to the distance to which a given dust particle will be carried by a wind of known velocity, it is known that the velocity of the wind decreases regularly downward until within about fifteen feet



of the surface of the ground. Within that distance of the ground the wind currents vary very irregularly.<sup>1</sup> On the other hand, the results obtained would be misleading if the platforms were placed at a great height above the surface, for then dust might be collected which would have traveled a considerable distance before falling to the ground. Platforms have been placed on the gable ends of barns during preliminary work, but this is unsatisfactory on account of the unknown effect of the building on the wind currents, and the possibility that dust formerly lodged in the roof may be blown onto the plates.

The number of plates exposed in one set, that is, on one platform at the same time, is determined by preliminary experiment, and is so selected that a sufficiently large sample of the dust will be obtained to admit of accurate weighing and analysis. It depends upon the soil and vegetation of the area in question, upon the distance from the plant, and upon the length of time of exposure. The writer has used sets of ten and twenty plates, and has found ten usually sufficient.

The choice of the time of exposure is optional within certain limits. Sets of twenty plates each are about as large as can be handled to advantage, and the time of exposure must be sufficient to allow the collection of an adequate sample under the existing conditions. On the other hand, the shorter the interval of exposure, the more accurately can the results be correlated with the corresponding wind direction and velocity records. The best plan is to use a short period of exposure, three to five days, repeatedly for a considerable length of time such as three to five weeks. In this way the results of each exposure can be compared with the corresponding wind conditions for detailed study, and the sum of the dust fall during the whole time of the investigation will show the total effect of a variety of wind conditions. The maximum time of exposure possible is set by the ability of the vaseline to retain its power of holding the dust that falls upon it. An experiment was carried out to determine this limit. Twenty plates were exposed on a platform about fifteen feet above the ground and near a dusty road. Five of these plates were left undisturbed for four weeks, five for three weeks, five were replaced by fresh plates at the end of two weeks, and five were replaced with fresh at the end of each week for four weeks. The dust collected on the fresh plates week by week was compared with that deposited upon those plates that were left untouched for two, three and four weeks. The results indicated that up to two weeks the plates held all the dust falling upon them, but that during the third week only about three-fourths of the dust falling was retained, and during the fourth week only about one-third. During the experiment the dust fall was heavy, amounting to between three- and four-tenths of a gram on five plates in one week. It is possible that with a lighter dust fall the holding power of the plates would be satisfactory through the third week, but it is probably unsafe to depend upon the accuracy of the results after an exposure of more

than two weeks, or one week in case of very heavy dust fall. It will be interesting to determine whether the decrease in the holding power of the vaseline surface is caused by simple exposure to air and sunshine, or whether it is dependent only upon the amount of dust which has lodged on the plate. The determination of this point can be carried out only by experiment, and since the experiment requires at least four weeks of continuous fair weather it will be some time before it can be completed.

The results of the field and laboratory work are obtained in terms of grams of dust deposited upon a given number of plates during a certain number of days, hours and minutes. For convenience in comparing the dust fall at different points it is necessary to express the results in terms of some selected unit. The most convenient unit is that of "pounds per acre per day." For some purposes it is interesting to calculate the results in terms of "tons per acre per year," but this latter unit is open to the objection that, since the experiments never exceed a few days in length, it presumes that the dust fall determined is constant throughout a year.

The simple determination of the total dust fall at given points does not afford sufficient information on which the distribution of the cement dust from a plant can be determined. It is necessary to separate the total dust fall into what may be termed "field dust," that is, the dust blown from the surface of the ground and normally present in the air, and "cement dust" proper. By "cement dust" is meant that solid material which issues from the stack of a cement plant. Since cement proper is prepared by the grinding of the clinker, it cannot be present in the dust, but the latter will consist of "raw mix," partially calcined but not fused, of a composition dependent upon the raw materials used and the construction of the kiln. The simplest method for separating the total dust fall into field and cement dust, is to subtract from the dust fall found near the plant that found at control stations located outside the possible path of the cement dust, and consider the difference to be cement dust. While simple, this method may be very misleading. It might be satisfactory if the topography, as well as the character of the soil and its use were uniform throughout the whole field under consideration. Such, however, is not likely to be the case. The dust fall at remote control stations is not necessarily that normal to the region near the plant, where the soil, agricultural and wind conditions may be very different, and some more accurate means of separating the dust fall into its components is required. This separation may be accomplished by the analysis of the samples, and on the basis of their silica and calcium oxide content. Cement dust contains much calcium, present either as oxide, carbonate or silicate, and relatively little silica, while field dust contains much silica and relatively little calcium. To carry out the calculation, it is first necessary to obtain a sample of the dust as it issues from the stacks of the plant, and determine the percentage of silica and calcium, usually expressed as calcium oxide, which is present. The samples col-

<sup>1</sup> Cf. Bull. 68, Bureau of Soils, pp. 41-44. Udden, *Jour. Geol.*, 2, 318.

lected in the field have been found, invariably, to contain more silica and less calcium oxide than the sample from the stacks, showing clearly the effect of the admixture of field dust. The percentage of silica increases, while that of calcium oxide decreases, with increasing distance from the plant. The silica and calcium oxide contents of the samples from the control stations are also determined. It is then possible, on the basis of the calcium oxide content, to calculate what mixture of cement dust and field dust, both of known calcium oxide content, will give the percentage of calcium oxide found in the sample obtained at any point in the field. The same calculation can be repeated on the basis of the silica content, and the results have been found to agree very closely. It is thus possible to separate the total dust fall at any point into "field dust" and "cement dust," with satisfactory accuracy. Two possible

dust. Calculations made in the same way on the basis of the silica content gave results in good agreement with those given in the table.

A number of important points are brought out very clearly by the data in Table I. It is apparent that the dust fall does not depend only on the distance from the cement plant. Thus D 34 at 2.8 miles shows a higher cement fall than D 25 at 1.2 miles. This is due, of course, to the difference in the direction from the plant. Sample D 34 was taken in the direction of the prevailing wind, while sample D 25 was taken to one side of this direction. If the wind conditions are fairly steady, the dust fall will often be restricted to a very narrow zone, but its length will depend upon the velocity of the wind. If the wind be light the dust will not travel far, but the dust fall will be heavy near the plant, while if the wind has a high velocity the dust will travel a great distance, but

TABLE I—DATA SHOWING DUST FALL IN THE NEIGHBORHOOD OF A CEMENT PLANT

Ref. No.	Distance from plant Miles	Number of plates	Time of exposure Days	Weight sample Grams	Pounds per acre per day	SiO <sub>2</sub> Per cent	CaO Per cent	Calculated cement dust Per cent	Calculated pounds per acre per day	
									Cement dust	Field dust
D 26	1.2	10	3.695	1.0152	10.9	17.92	47.95	95.5	10.4	0.5
D 22	1.2	10	8.142	2.0789	10.1	17.29	47.39	94.3	9.5	0.6
D 25	1.2	10	3.691	0.5261	5.6	19.58	44.61	88.3	4.9	0.7
D 33	1.7	10	3.843	0.5639	5.8	19.39	43.19	85.2	4.9	0.9
D 30	2.2	10	3.772	0.0611	0.7	34.86	31.09	59.1	0.4	0.3
D 31	2.0	10	3.771	0.1611	1.7	26.32	33.32	64.3	1.1	0.6
D 34	2.8	10	3.885	0.6344	6.5	18.52	45.17	89.5	5.8	0.7

sources of error in this procedure are apparent. It may be that the calcium oxide content of the dust from the control stations is not identical with that of the field dust near the plant. This possible error is unavoidable, but since the amount of calcium present in soil is low, and fairly uniform, it is not serious. The presence of cement dust from the plant in the soil near at hand, prevents the use of soil analyses to control this possible error. The presence of this cement dust in the ground introduces the second possible error referred to above. It may be that some of the cement dust collected on the plates was previously deposited on the ground, and was blown up onto the plates by the wind currents. This possibility cannot be avoided, but can only be minimized as far as possible by placing the plates well above the ground, and at points removed from dusty roads or open fields with cultivated surfaces.

Some of the results actually obtained in the field, the analytical data, and the percentage of cement dust in the sample calculated as explained above, are given in Table I.

TABLE II—EFFECT OF DEPOSITION OF SAND ON COLLECTING PLATES BY A FLURRY OF WIND

Ref No.	Conditions	No. of plates	Time of exposure Days	Weight sample Gram	Pounds per acre per day	SiO <sub>2</sub> Per cent	CaO Per cent	Calculated cement dust Per cent	Calculated pounds per acre per day	
									Cement dust	Field dust
49	Normal	10	2.948	0.5125	6.8	29.9	33.7	65.0	4.4	2.4
56	Wind flurry	6	2.958	0.5236	11.7	45.0	19.2	36.8	4.3	7.4

The results given in the last three columns of Table I are calculated from the data given on the basis that cement dust contains 50 per cent calcium oxide and that field dust contains 4 per cent of calcium oxide. This basis was determined by averaging analyses of cement dust, and of field dust obtained on plates exposed at such a distance and direction from the plant that there was no chance of its containing cement

the fall near the plant will be much lighter. It is apparent that the wind conditions must be thoroughly known before the results of field work can be properly interpreted.

Examination of Table I will disclose one very important point, namely, the relatively constant value for the fall of field dust, expressed in pounds per acre per day in the last column of the table. The average value for the field dust fall was 0.6 pound per acre per day, and the highest and lowest values differed from this by only 0.3 pound. This, too, in spite of large variations in the fall of cement dust. It is apparent, therefore, that this method permits the estimation of the fall of cement dust over and above the normal fall of field dust with satisfactory accuracy. The ability to eliminate disturbing factors by this method is also illustrated by the following case: The two results given below in Table II were obtained at the same place under very nearly identical weather conditions. The location was near an open sandy region. During the time of collection of the second sample there was a short period of high wind from

such a direction that a large amount of sand from this area was blown up onto the collecting plates. In spite of this interference, however, it is clear that the cement dust fall was nearly identical throughout the two periods.

It is interesting to compare the figures for dust fall which have been given with those which have been recorded in connection with great dust

storms. Such a comparison is given in Table III.

TABLE III(a)—COMPARISON OF DATA ON EUROPEAN SIROCCO DUST FALLS WITH THAT FOUND NEAR CEMENT PLANTS

DATE	PLACE	Weight of dust in pounds per acre per day
Oct. 16, 1846	Southeastern France	5.62
March 31, 1847	Tyrol	17.80
March 11, 1859	Westphalia	275.0
Feb., 1862	Salzburg, Austria	0.75
March 24, 1869	Carniola, Austria	44.7
March 19, 1901	Taormina, Sicily	24.1
March 9-12, 1901	Europe	32.4
	Maximum	3.02
	Minimum	10.9
1913 (by author)	California. Maximum in Table I	22.9
1912 (by author)	California. Maximum found near a cement plant	0.42
1913 (by author)	California. Lowest dust fall from a cement plant	

(a) The data used for comparison in this table were obtained from Bull. 68, Bureau of Soils, United States Department of Agriculture, and have been recalculated into terms of pounds per acre per day. Where only the date of the dust fall was given the time was assumed to be one day.

The question of the elimination of the loss of cement dust by the installation of proper devices at the plant does not come within the scope of this paper. It is sufficient to state that it can be accomplished, and that it is a matter of record that amounts in excess of fifty tons per day of cement dust have been recovered from a five-kiln plant in such a form as to permit its use in the manufacture of cement, and that the result has been advantageous to both the cement company and its neighbors.

#### CONCLUSION

In this paper the problem arising from the loss of large amounts of dust through the stacks of cement plants has been outlined. The methods available for the determination of the dust fall in the field have been stated and discussed. A practical method has been given in detail, and a method of calculation by which the cement dust can be distinguished from the field dust has been explained. The importance of a study of the wind and weather conditions as a preliminary to proper interpretation of the results of field work has been emphasized. Data have been presented which show the results obtainable by the methods given, and the relation of the dust fall near cement plants to that of certain great dust storms.

The writer wishes to express his indebtedness to Mr. G. S. Bohart, of this University, for his assistance in carrying out the analytical part of the work which has been presented.

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#### THE COMBUSTION METHOD FOR THE DIRECT DETERMINATION OF RUBBER<sup>1</sup>

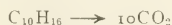
By L. G. WESSON

Received March 9, 1914

The method most in use at the present time for the determination of the caoutchouc content of rubber goods is an indirect one, in which the sample is analyzed for its moisture, mineral matter, sulfur, resin and other contents, these values being then added together and the sum subtracted from 100 per cent to arrive at the percentage of rubber present. As many of the best methods for estimating these constituents are admittedly inaccurate, the indirect method is not a satisfactory one. A number of direct methods

have been proposed and thoroughly tested, but as they depend for their accuracy on certain derivatives of rubber, the nitrosite, the nitrosate, and the tetrabromide, that have not thus far been obtained with unvarying composition, these methods have not found general acceptance either as technical or research methods for this extremely important estimation. It is hoped that the method<sup>1</sup> about to be described will lend itself to development not only as a dependable one for rubber research work, but also for the commercial laboratory.

The procedure, in brief, consists first in forming the nitrosite of rubber by the action of nitrogen trioxide gas upon a finely ground and acetone-extracted sample of the rubber suspended in chloroform. After the completion of the action, the insoluble nitrosite, fillers, etc., are filtered from the chloroform, and the nitrosite is dissolved in acetone. The suspension of finely divided mineral matter is then allowed to settle out, or is thrown down with the centrifuge. An aliquot portion of the solution is transferred with a pipette to a small flask, and its volume reduced by evaporation to a few cubic centimeters. This small volume of acetone solution of the nitrosite is now transferred with the help of ethyl acetate to a porcelain boat containing alundum, and, after the acetone and ethyl acetate have been expelled by warming the boat for several hours in a drying oven, the nitrosite is burned in a current of oxygen, and the carbon dioxide thus formed is absorbed in soda-lime and weighed. If all of the carbon originally in the sample as rubber, and only such carbon, reaches the soda-lime apparatus as carbon dioxide through the intermediate nitrosite, the equation



enables one to calculate the  $C_{10}H_{16}$  or real caoutchouc content of the sample.

PROCEDURE AND APPARATUS IN DETAIL—The procedure and apparatus employed in obtaining the results given later are the outgrowth of many trials and experiments. Doubtless deviations are allowable in many points, but there was not opportunity to study the effect of changing various factors.

The sample should be ground to pass a 20-mesh sieve, if possible, or cut up fine with the scissors if very soft. A weighed amount of the sample, 0.5 gram for compounds containing about 50 per cent or less of rubber, and 0.25 gram for those containing a higher percentage, is wrapped into a bundle with a 9 cm. filter paper and extracted for 3 to 4 hours with acetone in an apparatus of the Wiley or Cottle type, in which the sample is extracted by the solvent at the boiling point of the latter. The residue, from which the excess of acetone has been squeezed with the fingers, is then transferred to a 50 cc. calibrated, glass-stoppered flask and allowed to dissolve or swell up in about 40 cc. of chloroform,<sup>2</sup> which action may be hastened by warming the flask.

<sup>1</sup> A preliminary note on this method was published in THIS JOURNAL, 5 (1913), 398.

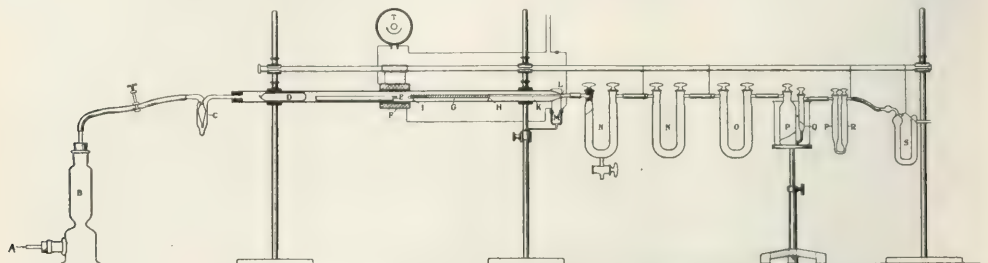
<sup>2</sup> The chloroform should not be previously dried, as moisture is apparently advantageous in giving a more rapid action of the nitrogen oxides on the rubber.

<sup>1</sup> Published by permission of the Director of the Bureau of Standards.



The rubber is now submitted to the action of nitrogen trioxide gas, evolved by running nitric acid of sp. gr. 1.3 dropwise on arsenic trioxide contained in a flask warmed in a boiling water bath. After the gases have been passed through an empty gas-washing bottle to condense most of the moisture and nitric

stoppering, for a half hour to ensure complete solution of the nitrosite in the acetone. The volume is now made exactly to the mark, the flask stoppered and shaken, and, to obtain a clear solution, the insoluble mineral matter is allowed to settle, or better, is quickly centrifuged out: 1500 revolutions per minute



APPARATUS FOR THE DIRECT DETERMINATION OF RUBBER BY THE COMBUSTION METHOD

- |  |  |  |
|--|--|--|
| A. Oxygen enters   | G. Platinum spiral about 10 cm. long (No. 20 wire)               | O. U-tube containing 30-mesh granulated zinc     |
| B. Moist soda lime   | H. Porcelain stem  | P. P. Soda lime                                  |
| C. Bubble counter containing sulfuric acid (Dennstedt)                             | I. Platinum leg for supporting stem                              | Q. Calcium chloride                              |
| D. Closed tube of Jena combustion glass, 8 cm. long, to prevent backward diffusion | K. Platinum leads 8 cm. long (No. 10 wire)                       | R. Alumina                                       |
| E. Porcelain boat  | L. Short platinum wires sealed into tube                         | S. U-tube containing palladium chloride solution |
| F. Heating coil of nichrome ribbon   | M. Mercury contacts  | T. Rheostat                                      |
|  | N, N. U-tubes containing glass beads and $\text{H}_2\text{SO}_4$ |  |
|  | K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>                    |  |

acid carried over from the generator, they enter the chloroform through a delivery tube joined by a rubber connection to the gas washing bottle, and fitting closely end for end to the same. The flask containing the chloroform should be immersed in a beaker of cold water during the reaction, since the solubility of the oxides of nitrogen in chloroform is increased and the danger of the gas exerting a partial oxidation of the rubber to  $\text{CO}_2$  is probably diminished thereby. The gas should be passed into the chloroform until a deep green color is obtained which is permanent for at least 15 to 20 minutes after the delivery tube has been disconnected from the gas generator.

The next morning the chloroform is decanted off, using gentle suction, through a small Gooch crucible provided with a mat of dry asbestos. If the filtrate is colored brown from the dissolved gases, one can be certain that a sufficient excess of the nitrogen oxide has been used. After the flask has been rinsed out several times with small volumes (5 cc.) of chloroform, each time decanting carefully through the crucible, the excess of chloroform and acid vapors which remain in the flask should be expelled by the passage for a few minutes of a gentle air current through the original delivery tube. If some nitrosite from the rubber connection is on the upper end of this tube, it may be easily removed by moistening it with acetone and wiping clean with a piece of filter paper.

The nitrosite in the crucible is then dissolved by placing the crucible in a 75 cc. beaker, adding successive small portions of acetone, and pouring each into the original flask until about 40 cc. have been used. No harm is done if a portion of the asbestos gets into the flask. In the meantime, the delivery tube has been freed from the nitrosite by sucking some of the acetone up into it from the beaker, and rinsing the outside into the same. Let the flask now remain in a beaker of water with occasional shaking, without

are sufficient to give a clear solution in from 5 to 10 minutes.

To regain the original temperature, the flask is now allowed to stand again in the beaker of water until the correct volume is once more attained. An aliquot portion of the solution (25 cc.) is now pipetted to a 50 cc. Erlenmeyer flask. To reduce the bulk of this solution to a few cubic centimeters, the flask is warmed in a dish of water while a current of air is blown into the flask. The acetone should not be completely expelled. The nitrosite is transferred from the Erlenmeyer flask to a porcelain boat 14 cm. long  $\times$  1.1 cm. wide, and about two-thirds full of alundum,<sup>1</sup> which is used to secure an even combustion of the nitrosite. The acetone solution of the nitrosite should not be poured into the boat, but should be drawn up into a small (2 cc.) pipette and run out evenly over the alundum. Several 2 to 3 cc. portions of ethyl acetate<sup>2</sup> are then used to rinse out the remainder of the nitrosite, using a small wash bottle and the pipette for this purpose. Ethyl acetate is used for the expulsion from the nitrosite of acetone which is otherwise retained in small amounts, perhaps mechanically by the nitrosite or by the portion of the mineral matter which passes in solution with the nitrosite into the boat, or by reaction with the nitrosite during drying. When enough wash liquid has been added to the boat to show above the alundum, the most of it should be expelled by placing the boat for a few minutes in the drying oven. The same procedure should be repeated at least once, using small portions of ethyl acetate in the transfer as described above. When one is certain that no nitrosite remains in the flask or pipette, the boat is dried for 2 hours at about 85° C.

<sup>1</sup> "RR" alundum, 90-mesh, specially prepared for carbon determinations. Norton Company, Worcester, Mass. A fresh portion should be used for each combustion.

<sup>2</sup> The so-called "absolute ethyl acetate" containing about 2 per cent of alcohol. It should be redistilled before use since it may contain other organic substances not easy to volatilize.

A circulation of air in the oven to carry away the acetone and ethyl acetate vapors will assist the drying greatly. The nitrosite is now ready for the combustion.

The combustion apparatus as it was finally developed, contains features already used outside of this laboratory,<sup>1</sup> and others original with either my colleagues or myself. The arrangement of the parts is best understood from the figure.

The tube is of Jena combustion glass, or better of quartz, 50 cm. long and 1.5 cm. bore. The nitrosite is decomposed by the heat of an external coil, made by winding two layers of nichrome ribbon,<sup>2</sup> leaving 0.1 cm. between the turns, on an asbestos-covered copper or brass tube, 5 cm. long and of such a diameter as to leave a 0.3 cm. space between the metal and the combustion tube; and then covering it with asbestos paper to form an insulating layer 1 cm. thick. During the combustion the coil as it moves forward should never be moved so fast that its forward end reaches more than 1 cm. beyond the border between the black carbon of the undecomposed nitrosite and the white alundum of the completely burned portion. The decomposition products are carried forward by the current of oxygen over a red-hot spiral of platinum wire which serves as the catalyzer for complete oxidation. The spiral is made from 1.3 meters of No. 20 wire wound into a cylinder 0.7 cm. in diameter, and is supported in the middle of the tube by an unglazed porcelain or clay stem 12 cm. long and 0.3 cm. in diameter, the return end of the spiral passing back through the stem. The leads for the spiral are 8 cm. long and are made with No. 10 platinum wire. One end of the pipe-stem is supported by these leads, and the other end by a small leg of platinum wire. The leads may connect with the outside in one of several ways. There may be a rubber stopper at the forward end of the tube through which are pushed two heavy copper, nickel, or platinum wires, the ends of which are bent into small loops into which the platinum leads are placed before the insertion of the stopper. Nickel is the better of the first two metals named. The platinum wires are good, as they may be sealed into small glass tubes which reach just through the stopper. In any case the stopper soon deteriorates, although this action has no noticeable effect on the results of the combustion. The most satisfactory method, however, consists in drawing down the forward end of the combustion tube as in the diagram, joining on a 3 cm. tube of 0.5 cm. bore, and sealing in two 3 cm. lengths of heavy platinum wire. These are bent up on the inside and the platinum leads are slid forward so as to rest upon them.

The oxides of nitrogen formed during the combustion of the nitrosite are absorbed by a saturated solution of potassium bichromate in concentrated sulfuric acid. Acid vapors and sulfur trioxide are held back by 30-mesh granulated zinc. Attention is called

to the form of apparatus in the figure for the absorption of carbon dioxide by soda-lime. The capillary tube makes a good substitute for a stopcock on account of its comparative lightness, and is effective in separating the moist soda-lime from the calcium chloride. Empty, the apparatus weighs 20 to 25 grams and will hold 35 grams of soda-lime,<sup>1</sup> and 7 grams of calcium chloride. It will absorb 10 grams or more of carbon dioxide without renewal. The second soda-lime tube contains alumina<sup>2</sup> in its second arm, which, it is thought, dries the gas to a degree comparable, for the purposes of the present work, to the drying by the concentrated sulfuric acid which precedes the soda-lime apparatus. To be certain that complete combustion is obtained, the gas finally passes through a faintly yellow solution of palladium chloride in water. While using the apparatus in its present form, it has not been necessary to renew the palladium chloride solution, no sign of reduction having appeared in a number of combustions. The sulfuric acid-bichromate solution must be renewed in the first U-tube after every two or three analyses, while the zinc will last for a larger number of determinations.

**CALCULATION**—If 0.5 gram sample, and 25 cc. out of 50 cc. of the acetone solution have been taken, the weight of CO<sub>2</sub> found multiplied by  $136/440 \times 4 \times 100 = 123.6$  gives the percentage of C<sub>10</sub>H<sub>16</sub> on the basis of C<sub>10</sub>H<sub>16</sub>  $\rightarrow$  10CO<sub>2</sub>.

**TIME REQUIREMENTS**—For a single nitration, about 15 minutes per sample are necessary; for the combustion, 30 to 45 minutes. Analyses of samples ground up in the forenoon of one day are completed the next. With one combustion tube, two analyses may be run per day along with other work, while by using two tubes it is thought that, after some proficiency has been acquired, as many as four determinations can be made per day.

**FORMATION OF CO<sub>2</sub> FROM THE RUBBER DURING NITRATION**—It is claimed by Alexander,<sup>3</sup> that during the formation of the nitrosite and nitrosate of rubber, large quantities of carbon dioxide are evolved from the oxidation of the rubber by the nitrogen oxides. Gottlob,<sup>4</sup> on the other hand, found only very small amounts of carbon dioxide. The writer made several tests of this important point by passing the gases from the rubber solution into a large volume of clear, saturated baryta water. Fine Para rubber, previously extracted with acetone and dried, was used for the experiments. After the chloroform, cooled as in the analytical procedure, had attained the deep green color, the apparatus was allowed to stand three to four hours, after which a current of carbon dioxide-free air was used to sweep into the barium hydroxide solution any carbon dioxide which might have formed during the interval. Only a trace of barium carbonate, a slight ring in the delivery tube, was formed, although the barium hydroxide solution remained alkaline throughout the experiment.

<sup>1</sup> The J. T. Baker Chemical Co. furnishes a 12 mesh soda lime containing 15 per cent water, prepared for carbon dioxide absorption.

<sup>2</sup> F. M. C. Johnson, *J. Am. Chem. Soc.*, **34** (1912), 911.

<sup>3</sup> *Z. anorg. Chem.*, **30** (1907), 1358; **34** (1911), 684.

<sup>4</sup> *Ibid.*, **20** (1907), 2213.

<sup>1</sup> The most important of these are the electrically heated platinum coil used as a catalyzer [Morse and Taylor, *Am. Chem. J.*, **33** (1905), 591], and the electrically heated external coil used for the decomposition of the substance to be burned.

<sup>2</sup>  $0.11 \times 1/2\pi$ , R = 1.3 to 1.5 ohms per ft., Driver Harris Wire Co., Harrison, N. J.

**DETERMINATION OF THE SULFUR OF VULCANIZATION**—If the statement of Alexander<sup>1</sup> proves to be true, that the sulfur of vulcanization of the rubber remains quantitatively in the nitrosite, this method could possibly admit of the simultaneous determination of the sulfur of vulcanization. An aliquot portion of the clear acetone solution of the nitrosite would be evaporated to dryness, and the sulfur determined in the usual way.

**RESULTS**—The following results were obtained by the method above described. All are given that have been obtained on good quality, soft-vulcanized compounds since the date after which no great changes in the procedure were made. Whether the method is applicable to compounds of poor quality has not been determined, and as the author is no longer in a position to work on this point the field must be left to others. This Bureau may be able, however, to work in this field at some later date.

- A. A washed and dried Up-river Fine gave 94.0, 95.1, 95.8 and 95.9 per cent  $C_{10}H_{16}$ .  
Average = 95.2 per cent plus 3.3 per cent acetone extract = 98.5 per cent.
- B. A commercial compound containing 45 per cent Fine Para gave 42.0, 42.2, 42.7, 43.1, 43.3 and 43.4 per cent  $C_{10}H_{16}$ .  
Average = 42.8 per cent plus 1.3 per cent acetone extract = 44.1 per cent.
- C. A commercial compound containing 48 per cent Fine Para gave 44.8, 45.1, 45.1 and 45.3 per cent  $C_{10}H_{16}$ .  
Average = 45.1 per cent plus 2.4 per cent acetone extract = 47.5 per cent.
- D. The same compound after standing finely ground for a month gave 43.4, 43.5, 43.5 and 43.0 per cent  $C_{10}H_{16}$ .  
Average = 43.7 per cent.
- E. A commercial compound containing 25 per cent Fine Para and 20 per cent Caecho or 45 per cent gum gave 40.3, 40.4, 40.6 and 41.1 per cent  $C_{10}H_{16}$ .  
Average = 40.6 per cent plus 3.2 per cent acetone extract = 43.8 per cent.
- F. A commercial compound containing 41.5 per cent Coarse Para gave 39.5, 39.6, 39.8 and 40.1 per cent  $C_{10}H_{16}$ .  
Average = 39.8 per cent plus 2.1 per cent acetone extract = 41.9 per cent.

#### SUMMARY

A new method for the direct determination of rubber is described, which is based upon the combustion of the nitrosite of rubber in a current of oxygen, and weighing of the carbon dioxide thus formed. The results indicate a fair degree of reliability for both raw rubber and high-grade vulcanized compounds. The use of this method for the analysis of low-grade compounds and for the simultaneous determination of sulfur of vulcanization may be possible if its application to these fields is further studied.

During this work many valuable suggestions were made by Dr. W. F. Hillebrand, Mr. J. B. Tuttle, and a number of others at this Bureau, and I take this opportunity to express to them my appreciation of the same.

DEPARTMENT OF STANDARDS  
WASHINGTON

#### OSAGE ORANGE—ITS VALUE AS A COMMERCIAL DYESTUFF<sup>2</sup>

By F. W. KIESMANN

#### INTRODUCTION

This study is the result of an investigation on the utilization of osage orange mill waste.

The trunk of the osage orange tree is rather small in size, misshapen, and generally defective as a saw

log; and, although because of the valuable properties of the wood (for wagon felloes especially) closer utilization will scarcely be found in the use of any other wood, comparatively large amounts of waste are produced annually.

Osage orange has long been used in Texas in a small way as a dyewood. The roots, bark, and wood are chipped and boiled with water and a more or less permanent yellow is obtained from the extract. Sargent<sup>1</sup> mentions the root bark as a source of a yellow dye and it has even been suggested by some<sup>2</sup> that osage orange is superior to fustic in its dyeing qualities, although no actual comparative experiments between fustic and osage orange seem to have been recorded.

In view of these facts, it seemed advisable not only to determine the chemical nature of the dyestuff but also its dyeing value as compared with the commercial dyewood it resembles most, namely, fustic.

A qualitative study of the aqueous extract obtained from the wood showed that the dyeing principles present were, as in fustic, morin or moric acid, and morintannic acid or maclurin. From a preliminary series of dyeing experiments made at this laboratory, it was found that osage orange, like fustic, is a poly-genetic mordant dyestuff.

Since the wood seemed to contain a sufficient amount of dye to give it commercial value, a series of comparative dyeing experiments on fustic and osage orange were arranged so as to determine as accurately as possible the value of osage orange in terms of a well-known standard such as fustic. In order to have these experiments performed at institutions best equipped for the purposes and also to obtain the results of a number of different workers in this field, the cooperation of a number of the leading textile schools<sup>3</sup> of the country was sought and the writer wishes to take this opportunity to thank them for their cooperation and assistance.

#### COMPARISON OF DEPTH OF COLORS PRODUCED

**REPORT E**—"It was noticed that dyeings produced with osage orange were weaker than those obtained with fustic under the same conditions. Since the osage orange produced a shade of color slightly different from the fustic in most cases, it is difficult to determine the exact relative strength of the two products. It seems, however, that the osage orange contains something like 20-25 per cent less coloring matter than the fustic."

**REPORT B**—"Dyeings were made under identical conditions on chrome mordanted worsted yarn with the same amounts of both the wood and solid extracts of both substances (*i. e.*, fustic and osage orange).

"The osage orange wood gave the heaviest shades

<sup>1</sup> Sargent, Chas. S. *Manual of the Trees of North America*.

<sup>2</sup> U. S. Dept. of Agr., *For. Serv. Cir.* 184, "Fustic Wood, Its Substitutes and Adulterants," by G. B. Sudworth and C. D. Mell.

<sup>3</sup> Philadelphia Textile School. New Bedford Textile School. Lowell Textile School. The North Carolina College of Agriculture and Mechanical Arts. Georgia School of Technology. Osage orange sawdust furnished by Mr. L. C. Bumpus, Farmersville, Texas.

<sup>4</sup> Reports on the experiments, giving the results of their test, were submitted by the coöperators, and the information given in this article is in the form of extracts taken from these reports. The reports are designated by letters, this designation being used to separate the extracts.

*J. Ind. Eng. Chem.*, 20 (1928), 1061; 24 (1932), 68; *Ind. Eng. Chem.*, 40 (1948), 1077.

<sup>5</sup> Presented at the 49th meeting of the A. C. S., Cincinnati, April 6-10, 1944.



but, like fustic wood, the yellow obtained had a reddish cast.

"With the extracts, the yellow obtained in each case was of a greenish tone; but that of the osage extract, while not so heavy as that given by the fustic extract, was of a much purer tone, the fustic being rather muddy."

REPORT A—"The dyeing properties of Old Fustic and osage orange are very similar, as will be seen by comparing the shades given on various mordants by the two dye-woods."

#### COMPARISON OF AMOUNT OF EXTRACT

REPORT C—"Upon extraction with water, osage orange sawdust was found to give a water-soluble extract in the proportion of 7.5 grams of extract for every 100 grams of sawdust."

REPORT B—"A sample each of the osage orange and of chip fustic was dried to constant weight and the moisture was found to be:

Osage orange sawdust	Per cent
Fustic	9.70

"The dried samples were then extracted with methyl alcohol and gave the following amounts of matter extractable with methyl alcohol:

Osage orange sawdust	Per cent of the dry sample
Fustic	26.63

"The residue in each case was then extracted with

shade of yellow, with chromium mordant a tan color, and with iron mordant a dark brown."

REPORT E—"The following table shows the results obtained by dyeing osage orange and fustic wood under the same conditions on wool mordanted with the indicated metallic salts:

PREPARATION OF WOOL SAMPLE	DYED WITH FUSTIC	TABLE I	
		DYED WITH OSAGE ORANGE	REMARKS
Unmordanted	Light yellow	Light yellow	Color produced of no value
Tin mordant	Light yellow	Light yellow	Color more pronounced than above. More reddish with fustic
Alum mordant	Bright yellow	Bright yellow	Yellower and brighter with the osage orange
Iron mordant	Dark olive	Dark olive	Not so deep and slightly greener with the osage orange
Chromium mordant	Orange yellow to old gold	Orange yellow to old gold	Fustic sample more reddish and deeper in tone than orange

#### FASTNESS TO LIGHT, WEATHER, WASHING, ETC.

REPORT E—"The colors produced by dyeing on alum and tin mordanted material were fairly good in appearance but were inferior in fastness to light, especially as compared with colors obtained with the first two salts (iron and chromium). Table II shows the result of test made on dyed samples of osage orange and fustic wood with respect to fastness to light and weather.

"It was noticed that the chrome mordanted samples showed a fastness in this respect superior to that of the other samples. The length of exposure necessary

TABLE II

	FUSTIC WOOD Time exposed			OSAGE ORANGE WOOD Time exposed		
	5 days	10 days	15 days	5 days	10 days	15 days
Direct dyeing	Faded	Color gone		Faded	Color gone	
Alum mordant	Slight fading	Faded		Slight fading	Faded	
Tin mordant	Slight fading	Faded		Slight fading	Faded	
Chromium mordant	No change	Very little if any change	Slight	No change	Very little if any change	Slight

water. The osage orange gave so little matter extractable by water that the amount was not determined. Fustic, on the other hand, gave 4.71 per cent of the dry weight. Therefore, the total extractable matter was:

Osage orange sawdust	Per cent
Fustic, 12.71 + 4.71	17.42

REPORT E—"The results obtained from experiments made clearly show that the osage orange product does contain a dyeing principle which is very similar in most respects to that found in fustic wood, and also this principle is found in a quantity sufficient to give the orange wood some commercial value as a dye-stuff."

#### CHARACTER OF DYEINGS

REPORT D—"It would appear that this substance (osage orange) could be advantageously used for self shades also in conjunction with logwood, other mordant dyes (*i. e.*, other natural mordant dyes), as well as with alizarine. Its dyeings are mono-chroic. If made in the form of a water extract it could be used for printing for yellows, browns, greens, and chocolates."

REPORT C—"It was found that this coloring matter was of a polygenetic character, giving, with a tin mordant, a comparatively bright shade of yellow, with aluminum mordant a somewhat duller and greener

to completely destroy the color in each case on the chrome mordant was not determined, it being simply noted that samples from each product showed very nearly the same resistance to fading for time exposed. During this time the fustic was possibly more affected than the osage orange in that there was a tendency for the color to lose some of its reddish cast.

"Samples dyed with fustic and osage orange were examined as to their fastness to washing tests, the samples in each case showing a fairly good fastness in this respect."

REPORT D—"This substance (osage orange) was found to dye level shades of good purity and brightness on wool mordanted with chromium in the usual manner. These dyeings show good fastness to light, water, and washing."

REPORT C—"These dyeings (with osage orange) were exposed to the light for a period of six weeks, and to combined light and weather for a period of 8 weeks. With both chromium and iron mordants the dyeings show very little change at the end of 5 weeks' exposure to sunlight. With aluminum and tin mordants the dyeings show the effect of sunlight in from one to two weeks, becoming much duller. The exposure of the sample dyed with the iron mordant to light and weather for 8 weeks shows very little change. That with chromium mordant for 8 weeks

loses its brilliancy to a considerable extent, although it does not become much lighter in color. The dyeings by aluminum and tin mordants are decidedly changed by this exposure to light and weather. The dyeings by chromium and iron mordants are sufficiently fast to prove of practical value, assuming that the coloring matter could be prepared cheap enough."

#### SUMMARY AND CONCLUSIONS

I—The quantity and quality of the dyestuff present in osage orange is almost identical with that of fustic.

II—Osage orange may be employed as a dyewood in all cases where fustic wood is used at present. The yellows produced by direct dyeing or by aluminum and tin mordants are too fugitive to be of commercial value. But the orange-yellows, old gold, deep tan, olive and chocolate shades obtained with chromium and iron mordants are equal to, if not better than, those obtained with fustic and are of sufficient fastness to be of commercial value.

III—A domestic source of a yellow dyewood has been found that can advantageously replace a foreign material used at present. The mill waste alone from the present manufacture of osage orange amounts to over 25,000 tons annually; and if this waste could be set down in the East for \$10 to \$12 per ton it is believed that it could compete successfully with fustic, both from cost of production and quality of color produced on dyeing.

FOREST PRODUCTS LABORATORY  
FOREST SERVICE, U. S. DEPARTMENT OF AGRICULTURE  
In Cooperation with the University of Wisconsin  
MADISON

### THE RESERVE SUPPLY OF PHOSPHATE ROCK IN THE UNITED STATES

By W. H. WAGGAMAN<sup>1</sup>

Received March 20, 1914

Numerous estimates have been made from time to time on the tonnage of phosphate rock available for future use in this country. These estimates vary so widely that little importance has been attached to them, and in many cases they can hardly be considered as anything more than wild guesses.

Owing to the pockety nature of many of our deposits of phosphorites or amorphous phosphates, careful surveys and thorough and systematic prospecting are necessary to gain anything like an accurate knowledge of their value and extent. The expenses of such examinations are frequently not warranted and are seldom made except immediately before actual mining operations are begun. Again, much of the phosphate property has been acquired so cheaply that only a superficial examination was necessary to justify its purchase. Under such circumstances the owners of the land may have but a hazy idea of the amount of phosphate contained therein. On the other hand, some of the phosphate deposits, such as those in our western states and in certain parts of Arkansas and Tennessee, are of such a character that fair approximations of their tonnage might be made by careful surveys.

<sup>1</sup> Scientist in Investigations of Fertilizer Resources.

For some time it has been obviously desirable that both producer and consumer should have some idea (even though a rough one) of the amount of phosphate rock still unmined in the United States. Again and again disquieting reports have been spread that our supplies of this mineral, so important to the American farmer, were being rapidly depleted, and that thereby the agricultural interests of this country would soon be seriously impaired. Alarm has also been caused by the fact that several phosphate companies are owned by European capitalists, and fears have been expressed that foreign capital is seeking to acquire control of the American deposits. It has been urged even that some legislation be enacted preventing the exportation of phosphate rock.

In order to show the actual basis for such reports and whether or not there is any real need for curtailing foreign shipments of phosphates, the data herein contained were collected and compiled with considerable care. The figures were obtained by correspondence and consultation with mine owners and operators, and by direct observation and field investigations of the various deposits throughout the country. So little development work has been done in Kentucky and Arkansas that the tonnages given for these states are thought not to be close; they are regarded, however, as ultra-conservative.

The estimates given below are for rock grading from 58 to 78 per cent "bone phosphate of lime." In the case of the low-grade phosphate in the West and the wash heaps of Florida, the material is figured to its equivalent in high-grade rock.

	Tons
Utah, Idaho, Wyoming and Montana:	
High-grade.....	2,500,000,000
High-grade equivalent of all grades.....	7,500,000,000
Florida:	
High-grade equivalent of all grades.....	354,300,000
High-grade equivalent of wash heaps.....	20,000,000
Tennessee:	
High-grade equivalent of all grades.....	115,075,000
South Carolina:	
High-grade equivalent of all grades.....	10,000,000
Arkansas:	
High-grade equivalent of all grades.....	20,000,000
Kentucky:	
High-grade equivalent of all grades.....	500,000
Total.....	10,519,875,000

The production of phosphate in 1912, according to the figures of the United States Geological Survey, was as follows:

	Tons
Florida.....	2,406,899
Tennessee.....	423,331 (a)
South Carolina.....	131,490
Western states.....	11,612 (b)
Total.....	2,973,332

(a) Includes production of Arkansas.

(b) Includes Utah, Idaho and Wyoming.

Even assuming that there are to be no new discoveries in this country and that the average consumption during the life of the phosphate fields will be three times its present consumption, there is sufficient to last for over 100 years provided proper mining methods are employed and means for utilizing the lower grade material are devised.

Another feature of the phosphate industry which in recent years has become of considerable interest to the operator, the fertilizer manufacturer, and the farmer, is the growing use of raw ground rock phosphate for direct application to the field. While the

value of this material as a fertilizer still seems to be an open question, many agronomists and agricultural chemists strongly recommend its use, supporting their recommendations by considerable data obtained by actual plot tests. In 1912 the annual consumption of raw ground phosphate rock, based on the amount marketed, was 48,365 tons. While this is less than 1.29 per cent of the total phosphate produced and only 4.01 per cent of that marketed in the United States, the sale of ground rock is becoming quite a factor in the phosphate industry.

BUREAU OF SOILS, WASHINGTON

#### DETERMINATION OF CARBON IN STEEL AND IRON BY THE BARIUM CARBONATE TITRATION METHOD<sup>1</sup>

By J. R. CAIN

The disadvantages attending the use of weighed absorption tubes as means for accurately determining carbon dioxide obtained during the combustion of steels and irons are in part as follows:

1—The elaborate precautions required to prevent change of weight of the tube due to gain or loss of moisture, necessitating complications in the purifying train before and after the furnace and the use throughout the apparatus of drying agents of the same hygroscopic power.

2—Difficulties in weighing large glass vessels caused by electrical effects in wiping, by buoyancy and by changes in temperature between balance room and laboratory.

3—The necessity for maintaining constant conditions with respect to the atmosphere within the tube, requiring sometimes a long period of aspiration after the combustion is completed.

4—The liability to error from access of gases containing sulfur and chlorine, which may be formed during combustion of the metal or of the carbonaceous residue therefrom.

5—The difficulty of determining whether the increase in weight of the tube is due solely to carbon dioxide.

6—The time lost in waiting for absorption tubes to reach a condition of equilibrium before weighing.

Those who have used absorption tubes for work requiring a high degree of accuracy know that neglect of one or more of the precautions indicated above may easily occasion errors ranging from several tenths of a milligram to one or more milligrams. It is evident, too, that if the complicated purifying train used with an absorption tube gets out of order, or if the tube itself introduces error in some of the ways enumerated, it may often be a difficult matter to locate and correct the trouble. It is not surprising, therefore, that methods dispensing with the use of weighed potash bulbs, soda-lime tubes and the like are beginning to be used extensively by steel analysis. Of such methods the weighing of the carbon dioxide in the form of barium carbonate precipitate directly or after conversion into sulfate have been much used, the sulfate

method abroad,<sup>1</sup> and the carbonate method in this country. Thus, of 62 prominent American laboratories (representing manufacturers, consumers and testing laboratories) 32 used the potash bulb, 24 weighed the carbon as barium carbonate, 3 titrated the excess of barium hydroxide, 2 used soda-lime tubes and one weighed an absorption tube filled with barium hydroxide.<sup>2</sup> It is evident, in estimating the carbon dioxide by weighing the barium carbonate precipitate, or the sulfate obtained from it, that the difficulties mentioned above as peculiar to weighed absorption tubes, except number four, are eliminated or minimized; access of sulfur trioxide would still tend to cause high results.<sup>3</sup> If, however, the barium carbonate is measured by filtering it off and titrating it against standard acid, due regard being had to proper conditions for filtration and washing, there is no likelihood of error from any of the causes enumerated. The principle of this method is described in most standard text-books on quantitative and volumetric analysis, but there seems to have been but little application in steel analysis. The purpose of this paper is to show the special suitability of this procedure for accurate and fairly rapid steel analysis, taking up in order the sources of error or difficulty and the means of avoiding or minimizing these, and finally giving the results obtained by a series of analyses of pure sugar and of Bureau of Standards analyzed irons and steels. Without further consideration it can be seen that the adoption of this method at once simplifies the purifying train required after the furnace; nothing at all likely to be present in the escaping gases can affect the results if we except finely divided oxides carried over mechanically as the result of a very violent combustion. No such oxides were noticed during this work or during the analyses of many other samples by different methods; if there is any reason to suspect their presence, a simple filter made by filling a U-tube with 20-mesh quartz, previously carefully washed with hydrochloric acid and water, will remove them.

The points involving sources of error which were investigated were: (1) completeness of absorption of the carbon dioxide, (2) amount of washing necessary to remove the excess of barium hydroxide, (3) solubility of barium carbonate in the wash water, (4) exclusion of extraneous alkaline substances. In addition there were devised (5) means for the rapid filtration and washing of the barium carbonate with exclusion of carbon dioxide from the air.

1—COMPLETENESS OF ABSORPTION—This was established by burning sugar in amounts giving approximately the weights of carbon dioxide obtained during steel analysis, comparing the percentages of carbon obtained with the theoretical. As a further check two 8-bulb Meyer tubes (shown in  $1/10$  size in Fig. 1)

<sup>1</sup> Bauer and Deiss, *Probenahme und Analyse von Eisen und Stahl*, 1912, p. 121.

<sup>2</sup> Data communicated to the author as member of a technical committee on steel analysis.

<sup>3</sup> There is but little likelihood of  $\text{SO}_2$  being produced in burning steel and iron. Any small amounts of  $\text{BaSO}_3$  resulting thereby would be removed by washing (see Sec. 5 on Filtration and Washing), the solubility of  $\text{BaSO}_3$  being approximately 0.02 gram per 100 cc. of water at 20° (Seidell, "Solubilities of Inorganic and Organic Substances," 1907).

<sup>1</sup> Published by permission of the Director of the Bureau of Standards. Presented at the Cincinnati Meeting of the American Chemical Society April 6-10, 1914.



were worked in series. So long as a moderate rate of bubbling was maintained no cloudiness was ever observed in the second tube. In this connection, McCoy and Tashiro<sup>1</sup> have shown that  $1.0 \times 10^{-7}$  grams of  $\text{CO}_2$  can be recognized as a turbidity. If, however, the oxygen is passed too rapidly, particularly when burning steels containing more than 1 per cent carbon, some  $\text{CO}_2$  may reach the second tube. The proper rate of gas current to retain all the  $\text{CO}_2$  in the first tube is easily established by the operator after a few trials.

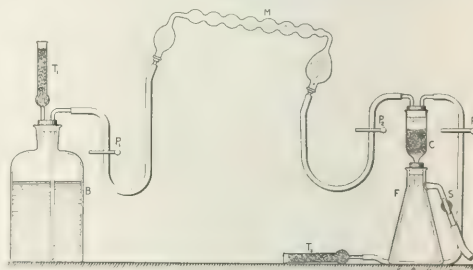
2—AMOUNT OF WASHING NECESSARY—Barium carbonate itself reacts alkaline to phenolphthalein, consequently this indicator cannot be used to show when all of the barium hydroxide has been removed. The practical question as to how much washing was necessary was decided by washing the barium carbonate obtained from the combustion of accurately weighed amounts of sugar until results agreeing with the theoretical, within a small experimental limit, were obtained. The amount of wash water thus determined was increased by 25 per cent. About 150 cc. wash water were usually found sufficient. The results are summarized in the recommendations later, under the head "Filtration and Washing of the Barium Carbonate."

3—SOLUBILITY OF BARIUM CARBONATE IN WASH WATER—The possible effect of the slight hydrolysis of the barium carbonate in causing low results by solvent action of the wash water was studied by comparing the results obtained when determining the barium carbonate from the combustion of the same weights of sugar, first by washing as above described, and then with twice and three times the amount of water recommended. The results showed that the error from hydrolysis is negligible for present purposes. (See table and footnotes *c* and *d*, p. 467.)

Holleman<sup>2</sup> found the solubility of freshly precipitated  $\text{BaCO}_3$  in  $\text{CO}_2$ -free water to be 1 part  $\text{BaCO}_3$  in 64,070 parts water at  $8.8^\circ$  and 1 part in 45,566 parts water at  $24.2^\circ$ , or approximately 1 part in 50,000 at the temperature of the laboratory during this work, *i. e.*,  $20^\circ$  to  $22^\circ$ . On this basis 150 cc. wash water (see preceding section) would dissolve about 0.0003 gram  $\text{BaCO}_3 = 0.000018$  gram carbon. This would be negligible for present purposes, and the amount dissolved would be really less than this because of the repression of solubility during the first washings by the barium hydroxide still present; also it is quite possible that in the rapid passage through the filter there has not been sufficient time for the wash water to become saturated with barium carbonate. Holleman's results are in good agreement with those of Bineau.<sup>3</sup> Holleman called attention to the fact, also recorded by Bineau, that the presence of carbon dioxide in water appreciably raises the solubility of barium carbonate and Holleman explains in this way the solubility of 1 part in 14,137 parts of water observed by Fresenius, who left the carbonate in contact with water exposed to the air for several days.

4—POSSIBLE SOURCES OF EXTRANEOUS ALKALINE SUBSTANCES—These are: (a) substances derived by action of water on the bottles containing the  $\text{CO}_2$ -free water mentioned later; such action should be avoided by choosing a good quality of glass bottle; Jena glass containers were found satisfactory; (b) alkali carried over mechanically from soda-lime guard-tubes by the air used to force out  $\text{CO}_2$ -free water; thick plugs of glass wool will remove this source of danger; (c) action of barium hydroxide on the walls of the Meyer tubes; these tubes should not give up alkaline substances to the standard acid after barium hydroxide has stood in them for  $1\frac{1}{2}$  hour and the tubes have then been thoroughly washed with alkali-free water; (d) action of barium hydroxide on filtering material; glass wool as a filling material is absolutely excluded on this ground; quartz has been found very satisfactory (see description of filtering apparatus); amphibole asbestos for the felt was found suitable from this standpoint as well as because of its resistance to attack by  $\text{N}/10$  hydrochloric acid.

5—FILTRATION AND WASHING OF THE BARIUM CARBONATE—This is carried out with the apparatus shown in the figure. The cut is approximately one-tenth size



APPARATUS FOR FILTERING BARIUM CARBONATE  
FIG. I

and is self-explanatory. *S* is a two-way stopcock connected to the suction pipe. The rubber tubing connected to the Meyer tube should be of best grade black rubber, and the lengths used should be chosen so as to permit of easy manipulation of the tube. The Meyer tube is connected or disconnected by the rubber stoppers which are left always attached to the rubber tubes. The carbon filter *C* is fitted with a perforated porcelain plate, sliding easily. The funnel is prepared for filtrations by making a felt of asbestos on the porcelain disc, using asbestos which has been digested for several hours with strong hydrochloric acid and then washed free of acid. On top of the asbestos is placed a layer of similarly washed quartz of the height shown in the figure. A mixture of grains of various sizes (approximately 50 per cent passing a 20-mesh and the remainder passing a 10-mesh and remaining on a 20-mesh sieve) is suitable. A mixture of quartz and asbestos works well and may be simply obtained by filling the funnel with a suspension of asbestos and delivering the quartz to the funnel from a beaker by means of a strong jet of water from the wash bottle, while maintaining a gentle suction. In this way the asbestos is properly mixed with the

<sup>1</sup> Orig. Communication, 8th Int. Congr. Appl. Chem., 1 (1912), 361.

<sup>2</sup> *Z. physik. Chem.*, 12 (1893), 135.

<sup>3</sup> *Ann. chim. phys.*, [3] 61, 290.

quartz. Proper attention to these details will be found to greatly expedite filtration. The stopper is now inserted in the funnel, the Meyer tube connected as shown, and the liquid and precipitate sucked into the funnel. Only very gentle suction should be used. When necessary,  $P_3$  is opened to admit air back of the column of liquid in the Meyer tube. When the contents of the tube have all been transferred, the large bulb nearest  $B$  is half-filled with water by opening  $P_1$ ; the stopcock  $S$  is operated during this and subsequent operations so as to maintain a gentle suction.  $M$  is now manipulated so as to bring the wash water in contact with all parts of the interior, after which the water is sucked out through  $C$ ;  $P_2$  is left open during this and subsequent washings. After eight washings, as directed, allowing the wash water to drain off thoroughly each time before adding more,  $M$  may be detached, the stopper removed from the funnel and the washing completed by filling  $C$  to the top with  $\text{CO}_2$ -free water, sucking off completely and repeating the operation once. Air is now admitted through the side opening of  $S$ ,  $C$  is removed and the porcelain disc carrying the quartz asbestos and barium carbonate is shoved, by means of a long glass rod, into the flask used for titrations, removing from the sides of  $C$  any adhering particles by a jet of water from the wash bottle.

#### APPARATUS FOR COMBUSTION

**APPARATUS**—The method requires no modification of any of the accepted appliances for the combustion of iron and steel. In the present work both gas and electrically heated furnaces were used. As already stated, there was no purifying train after the furnace, the Meyer tube being directly attached. Before the furnace was an electrically heated porcelain tube filled with copper oxide; then a calcium chloride tower filled with stick potassium hydroxide. Steels and irons were burned on a bed of alkali- and carbon-free alundum contained in a platinum boat. The blanks obtained by carrying through a complete determination, including filtration, washing, etc., but with omission of any carbon-containing substance, were usually 0.0 cc. and never more than 0.05 cc. of  $N/10$  hydrochloric acid, showing not only that the oxygen was sufficiently purified and the apparatus in good condition, but that the operations of filtration, washing, etc., introduced no appreciable positive error.

#### SOLUTIONS USED

**TENTH-NORMAL HYDROCHLORIC ACID**—Standardized by any of the accepted methods, or as follows: 20 cc. of the approximately  $N/10$  acid are measured out with a pipette, 5 cc. of nitric acid (1 to 1 by volume) added, and the silver chloride precipitated by an excess of silver nitrate solution in a volume of 50 to 60 cc. After digesting at  $70^\circ$  to  $80^\circ$  until the supernatant liquid is clear, the chloride is filtered off on a tared Gooch filter and washed with water containing 2 cc. of nitric acid per 100 cc. of water until freed from silver. After drying to constant weight at  $130^\circ$ , the increase of weight over the original tare is noted and the strength of the hydrochloric acid calculated on the basis of the weight of silver chloride thus ob-

tained, afterwards adjusting to the strength prescribed. Several concordant determinations with varying amounts of acid should be made. 1 cc.  $N/10$   $\text{HCl} = 0.0006$  gram carbon.

#### TENTH-NORMAL SODIUM HYDROXIDE SOLUTION

Standardized against the hydrochloric acid solution, with methyl orange as indicator. This solution is conveniently stored in a large glass bottle fitted with a soda-lime guard tube and arranged for delivering the solution by air pressure.

**METHYL ORANGE**—0.02 gram dissolved in 100 cc. of hot water and filtered.

**BARIUM HYDROXIDE SOLUTION**—A saturated solution filtered and stored in a large reservoir from which it is delivered by air pressure, protecting from carbon dioxide by a soda-lime tube. Three or four small bulbs of the Meyer tube are filled, and  $\text{CO}_2$ -free water is added until the remaining small bulbs are filled. When burning products high in carbon the stock solution may be used undiluted.

**CARBON DIOXIDE-FREE WATER**—This is conveniently made by passing air for a sufficient length of time through a soda-lime tube and into a 6- or 8-liter bottle filled with pure distilled water. The water is delivered by  $\text{CO}_2$ -free air under pressure.

#### THE METHOD

The combustion is carried out in the usual manner, care being taken not to pass the oxygen too rapidly. After filtering, washing and transferring the contents of the filter to a flask, as described under "Filtration and Washing of the Barium Carbonate," a slight excess of the standard acid is added from a burette, using a portion to rinse out the Meyer tube, and the excess of acid is then titrated against the sodium hydroxide, using methyl orange as indicator.

#### RESULTS OBTAINED BY BARIUM CARBONATE TITRATION METHOD

Material	Weight Gram	Carbon present Gram	Carbon found Gram	Difference Gram
Sugar(a).....	0.0100	0.00421	0.00427(c)	+0.00006
	0.0100	0.00421	0.00420	-0.00001
	0.0100	0.00421	0.00430	+0.00010
	0.0200	0.00842	0.00840	-0.00002
	0.0200	0.00842	0.00860	+0.00018
	0.0200	0.00842	0.00860	+0.00018
	0.0300	0.01263	0.01280	+0.00017
	0.0300	0.01263	0.01280	+0.00017
Bessemer Steel B. S., No. 23.....	1.000	0.00805(b)	0.00805	0.0000
	1.000	0.00805	0.00805	0.0000
	1.000	0.00895	0.00805	0.0000
Bessemer Steel, B. S., No. 10b.....	1.000	0.00373(b)	0.00372	-0.00001
	1.000	0.00373	0.00372	-0.00001
	1.000	0.02726(b)	0.02710	-0.00016
Pig Iron C, B. S., No. 5b.....	1.000	0.02726	0.02710	-0.00016

Mean error, sugar..... +0.000094

Mean error, steels and iron..... -0.000056

(a) B. S. Standard Sample No. 17. A 1% aqueous solution was made and the required amounts were delivered into a porcelain boat from a burette. After careful evaporation of the water the sample was burned.

(b) Certificate values.

(c) Washed with double the usual amount of wash water. The second portion of wash water was titrated against the  $N/10$  hydrochloric acid; the amounts used after deducting the blank when titrating the same quantity of the water used for washing were 0.10 cc. and 0.15 cc.

(d) Washed with three times the usual amount of wash water.

The results given in the table show that the method is as accurate as the weighing methods. It is not so subject to disturbing influences and requires less elaborate apparatus than those methods do.

#### NOTES AND PRECAUTIONS

1—After a little practice a precipitate can be filtered and prepared for titration in five minutes.

2—When working with steels high in carbon (above 1%) it is advisable not to use more than one gram, in order that filtration may be sufficiently rapid.

3—For very accurate work the Meyer tubes should be washed with dilute acid before beginning work each day. After a determination is finished, the Meyer tube should be completely filled two or three times with tap water, then rinsed with distilled water, in order to remove the carbon dioxide liberated when dissolving the carbonate from the previous determination.

4—The flask containing the carbonate should be very thoroughly agitated after adding the acid, since the carbonate sometimes dissolves rather slowly if this is not done; this is particularly the case if it has packed much during filtration.

5—The rubber tube connecting *B* (see figure) to the Meyer tube should be washed with a little water from *B*, before beginning determinations each day.

I am indebted to Mr. H. L. Cleaves of this Bureau who prepared the drawing of the filtering apparatus and made many determinations on steels which will appear in a later publication.

BUREAU OF STANDARDS  
WASHINGTON

#### THE DETERMINATION OF AMMONIA IN ILLUMINATING GAS<sup>1</sup>

By J. D. EDWARDS

Received March 21, 1914

This paper is a summary of the results of a brief investigation of the apparatus and methods employed for the commercial determination of ammonia in illuminating gas. A fuller report will be found in Bureau of Standards' *Technologic Paper No. 34*, and the application of this work in the form of operating directions for carrying out the determination will be included in Bureau of Standards' *Circular No. 48*, "Standard Methods of Gas Testing."

The method generally used for the determination of ammonia in purified illuminating gas depends upon the absorption of the ammonia in a standard acid solution, the amount of ammonia absorbed from a measured volume of gas being determined either by titration of the acid remaining unneutralized, or less frequently by allowing the gas to pass until the change in the indicator used shows that all the acid has been neutralized.

The choice of the proper indicator to use for this determination is of greater importance than the choice of apparatus, since the use of an unsuitable indicator may introduce large errors, amounting in extreme cases to more than one hundred per cent. Many indicators have been and still are commonly used which are not at all suited to the purpose, failing to meet one or more of the following essential requirements:

1—It should show a sharp end point in dilute solutions.

2—It should be sensitive to ammonia and not be seriously affected by ammonium salts.

3—The end point should be affected as little as possible by carbon dioxide.

The indicators which were found to be most suitable for the determination of ammonia in gas were sodium alizarinsulfonate, cochineal and paranitrophenol. Sodium alizarinsulfonate is less sensitive to carbon dioxide than either cochineal or paranitrophenol and gives a color change from greenish yellow to brown which is quite sharp even with very dilute solutions. Sodium alizarinsulfonate was the indicator used in the remaining experimental work. Methyl orange, though less sensitive to carbon dioxide than the above indicators, does not give sufficiently sharp color changes with weak solutions. Phenolphthalein and litmus, of course, are too sensitive to carbon dioxide to be of use here.

The presence of glass beads which are used in some of the absorption apparatus may lead to erroneous results for two reasons: (1) The beads may yield alkali on contact with the absorbing liquid; (2) washing of the beads may be incomplete. Although the absolute amount of alkali which might be dissolved from the beads is small, it may be equivalent to a considerable percentage of the total amount of ammonia to be absorbed. For this reason, it is recommended that the operator test the solubility of any beads he may use. The method of washing out the apparatus should also be tested to insure complete washing with a minimum of wash water.

Five different forms of apparatus were tested: The Referees apparatus, the Emmerling tower, the Lacey apparatus, the common form of gas wash bottle and a modified form of the Cumming wash bottle. This latter form (Fig. 1) was designed at the Bureau

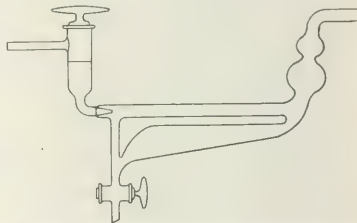


FIG. 1—MODIFIED CUMMING WASH BOTTLE (ONE-FOURTH SIZE)

of Standards for this work. In this form, the gas passing through the small nozzle acts like an injector and circulates the liquid rapidly and continuously, thus bringing fresh acid into contact with the gas.

The relative efficiency and from this the probable accuracy of the different forms of apparatus was determined by running the different forms in parallel, using gas from a common supply. A  $N/50$  solution of sulfuric acid was used as the absorbing agent. It was not considered desirable to use a stronger solution than this because of the small amount of ammonia to be absorbed and the fact that small errors in the measurement of stronger solutions make a large error in the ammonia apparently absorbed.

As a result of this comparison it was found that the Emmerling tower gave results which were somewhat higher than those obtained with the other forms and that the wash bottle gave results consistently lower.

<sup>1</sup> Published by permission of Director, Bureau of Standards. Abstract of paper presented at the Cincinnati Meeting of the American Chemical Society, April 6-10, 1914.



In a series of 10 tests, in each of which four different apparatus were run in parallel, the maximum difference between the high and low results of each test (expressed as a percentage of the average) was 8.3 per cent and the average difference 4.5 per cent. The ammonia content of the gas was varied from 1 to 20 grains per 100 cubic feet. (For full experimental details, see *Technologic Paper No. 34*, above referred to.)

A series of tests in which the gas after passing through the first absorption apparatus passed through an Emmerling tower, showed, in general, that the amounts of ammonia escaping the first apparatus but absorbed in the Emmerling tower were not detectable within the limits of error of the titration.

With careful operation, any one of the five forms of apparatus tested would ordinarily give results that are well within the limits of accuracy required for this determination, either for commercial control work or for the purpose of gas inspection. The wash bottle appears to be slightly less efficient as an absorber than the other forms, but still it gives satisfactory results. It is difficult to make any comprehensive statement defining satisfactory results. In general, results on gas containing up to about 5 grains of ammonia per 100 cubic feet should be within 10 per cent of the ammonia content of the gas, although the percentage error may be greater when the ammonia is 1 grain or lower. With gas containing more than 5 grains ammonia, the percentage error should decrease somewhat.

BUREAU OF STANDARDS, WASHINGTON

## THE STUDY OF THE CRUDE PETROLEUM FROM BIORITSU, FORMOSA

By TETSU. KATAYAMA

Received April 1, 1914

Favorable indications of petroleum deposits have been found in Formosa Island in many districts along the western slopes of the middle mountain range. Of these oil deposits that at Shukkokosio, about seven miles south of Bioritsu station on the main railway line in the island, is the most important, and is now worked by the Howden Petroleum Company. It is reported that about 3,000 gallons of crude petroleum are obtained daily from a single well there.

Several years ago the author studied the physical properties of this crude petroleum and found that the kerosene oil obtained from the crude petroleum by the ordinary method can not be used for lamp oil, the flame being very smoky. Further study had to be postponed, but in May, 1913, it was again resumed. By means of acetic anhydride, the smoky constituent was isolated and its nature studied, and it was at last found that the kerosene oil may be refined by changing the temperature and duration of the reaction on ordinary sulfuric acid treatment. The results thus obtained are submitted below.

### I—GENERAL PROPERTIES OF THE CRUDE PETROLEUM

The crude petroleum is a clear, mobile, brownish oil of specific gravity 0.831 at 15° C.; its smell is rather agreeable; it solidifies at 0° C.

FRACTIONAL DISTILLATION—300 cc. of the crude petroleum were introduced into a side tube distilling flask of about 500 cc. capacity, and distilled, the heat being so regulated that about 2.5 cc. of distillate passed over per minute. The average results of duplicate distillations are the following:

Fractions °C.	Per cent by volume	Sp. gr. at 15° C.
below 100.....	1.5	0.7770
100-125.....	15.8	0.7980
125-150.....	21.8	0.8155
150-175.....	12.2	0.8205
175-200.....	8.8	0.8360
200-225.....	7.8	0.8585
225-250.....	7.6	0.8790
250-275.....	7.5	
275-300.....	4.3	
Residue.....	13.2	

Solidifies at ordinary temperature

It is remarkable that the specific gravity of each fraction of this crude petroleum was very high—much higher than that of the corresponding fraction of other crude petroleum.

BURNING TEST—The kerosene fraction, distilling between 150° C. and 275° C., was refined with concentrated sulfuric acid by the ordinary method, washed with water several times, then with a dilute alkali solution, and again with water until the oil became free from acid and alkali. The kerosene oil thus refined was burned in a lamp of ordinary construction, but the flame was very smoky.

TEST FOR NITROGEN AND SULFUR—The crude petroleum was heated to boiling for a long time with some small pieces of metallic sodium, in a flask equipped with a reflux condenser. After cooling, the sodium was tested for cyanocompounds and sodium sulfide, but no test for either of these compounds was obtained.

### II SOLUBILITY OF THE CONSTITUENTS OF THE CRUDE PETROLEUM

At first an attempt was made to isolate the smoky constituent in the petroleum by distillation, but it was impossible. Every fraction separated by cautious fractional distillation gave a smoky flame. Then an attempt was made to separate the smoky constituent by a solvent. Edeleanu suggested that aromatic compounds and other hydrocarbons, rich in carbon atoms, may be dissolved away from the oil by liquefied sulfur dioxide, and Prof. Engler recommended this method as effective.<sup>1</sup> It was considered desirable to try this method, but the temperature of the laboratory at that time, always above 30° C., did not permit of this procedure. Therefore another solvent, which would extract the smoky constituent from the petroleum at ordinary temperature, was sought, and at last it was found that acetic anhydride was most suitable for this purpose.

EXPERIMENT I—250 cc. of the fraction distilling between 150° C. and 275° C. were introduced into a separating funnel and acetic anhydride was added, little by little, shaking well between each addition. At the beginning the added acid dissolved in the petroleum, but when 60 cc. of acid had been added the fluid separated into two layers, the lower layer being 9 cc. After the lower layer was drawn off, 10 cc. more of the acid were added to the upper layer, when 27 cc. separated as a lower layer. The lower layer was drawn

<sup>1</sup> *Ztschr. angew. Chem.*, 1913, p. 177

off and added to the formerly separated fluid. These operations were repeated until 200 cc. of acid had been used. Then the total fluid drawn off was 295 cc., while the residual upper layer was 155 cc. Both the fluids were washed well with water until they became free from acid, when the oil in the upper layer was 140 cc. and the oil in the tapped fluid was 110 cc.; that is to say, the upper layer contained 140 cc. of oil and 15 cc. of the acid, while the lower layer contained 110 cc. of oil and 185 cc. of the acid. These results showed that the petroleum contains two different constituents, one immiscible with acetic anhydride and the other easily soluble in acetic anhydride. Their specific gravities at 30° C. are:

The fraction before the treatment . . . . .	0.830
The immiscible oil . . . . .	0.804
The oil easily soluble in acetic anhydride . . . . .	0.864

It might be thought that these two constituents would have different boiling points, but the distillations of these constituents showed that their boiling points were the same.

The burning quality of these two constituents was next tested; the oil with the lower specific gravity burned brilliantly while the other gave a very smoky flame.

From the above experiment it was evident that the constituent which gives a smoky flame on burning may be separated from the petroleum by this difference of solubility in acetic anhydride. This separation depends, of course, upon the difference of solubility in acetic anhydride; it varies according to the quantity of the added acetic anhydride, and the method of adding. Though it was, of course, impossible to separate these constituents from each other absolutely, the division was sufficiently complete for practical purposes.

**EXPERIMENT 2**—The above experiment was repeated for the crude petroleum and every fraction of it. To 100 cc. of each fraction of the oil, acetic anhydride was added little by little, and the quantity of the acid used when the mixture just separated into two layers was noted. When the added acetic anhydride reached 100 cc. the quantities of the two layers, and the quantities and specific gravities of the oils contained in these two layers were determined.

#### SEPARATION OF THE OIL AND ITS FRACTIONS BY ADDING 100 CC. OF ACETIC ANHYDRIDE

Fractions Temp. in ° C.	Sp. gr. original oil at 30° C.	added when layers formed cc.	UPPER LAYER		LOWER LAYER		
			Total vol. cc.	Sp. gr. oil at 30° C.	Total vol. cc.	Sp. gr. oil at 30° C.	
Crude petro- leum.....	0.8215		67.5	63.0	0.804	132.5	0.8515
Residue above 250 .....	0.877		86.0	80.0		114.0	20.0
225-250 .....	0.848	13.3	83.0	78.3	0.823	117.0	24.5
200-225 .....	0.824	15.0	75.0	68.0	0.808	125.0	32.0
175-200 .....	0.809	30.0	70.0	60.0	0.796	130.0	40.0
150-175 .....	0.795	66.0	46.0	36.0	0.788	154.0	64.0

Lower fractions were more soluble in acetic anhydride than higher fractions, and fractions boiling below 150° C. gave no separations into layers when large amounts of acetic anhydride were added. The constituents in these fractions could be separated by dissolving in acetic anhydride and adding water, drop by drop. The fluid separated at first into two layers, then

into three layers, of which the lowest did not contain oil; the middle layer contained the smoky constituent and most of the acid, while the upper contained the non-smoky constituent and a little acid.

#### III. PROPERTIES OF THE SMOKY CONSTITUENT

The fraction boiling between 150° and 250° C. was mixed with half its volume of acetic anhydride and separated into its two constituents by the above described method; the oil obtained from the upper layer burned brilliantly, while the oil from the lower layer burned with a very smoky flame.

	Original fraction	Smoky constituent	Non-smoky constituent
Sp. gr. at 15° C. . . . .	0.830	0.855	0.822
Refractive index at 20° C. (Abb.) . . . . .	...	1.4932	1.4437
Iodine number (Hubl.) . . . . .	...	0.76	0.37

The low iodine numbers showed the comparative absence of open chain unsaturated compounds.

**NITRATION TEST.**—Concentrated nitric acid acts upon all the unsaturated compounds at a low temperature. A mixture of 20 grams of sulfuric acid (sp. gr. 1.84) and 16 grams of nitric acid (sp. gr. 1.375) was introduced into a small graduated cylinder equipped with a glass stopper: 10 cc. of the oil were added and mixed slowly, avoiding rise of temperature by cooling with water. After standing, the fluid separated into three layers: the upper layer contained non-reacted oil and a small quantity of nitrated substance; the middle layer consisted of nitrated oil and acid mixture; the lower layer consisted of the acid mixture and a little nitrated substance. The upper layer was separated, washed well with water and dilute alkali solution, and measured; this oil contained a small quantity (2-3 per cent?) of nitrated substance which was considered practically negligible. This volume was subtracted from 10 cc. and the difference was recorded as the volume of the nitrated portion in the fraction.

Percentages	Fraction before separation	Smoky constituent	Non-smoky constituent
Nitrated portion . . . . .	42	73	36
Non-nitrated portion . . . . .	58	27	64

The smoky constituent contained much nitrifiable portion. The specific gravities of both the non-nitrated portions obtained from the smoky constituent and the non-smoky constituent were 0.804 at 30° C. and both the non-nitrated portions burned brilliantly in an ordinary lamp. From these results, it was concluded that the nitrifiable oil was the cause of the smoky burning.

The nitrated portion obtained from the fraction boiling below 115° C. was reduced with hydrochloric acid, and metallic tin and excess of an alkali solution were added to it and distilled. A colorless oily substance with anilin-like odor was obtained. This substance was slightly soluble in water; the solution turned violet gradually on being exposed to air; the same change of color occurred also when bleaching powder solution was added; this substance formed a difficultly soluble crystalline salt with dilute sulfuric acid. These facts indicated that the substance contained aniline and its higher homologues.

**REACTION WITH PICRIC ACID.**—Picric acid forms crystalline compounds with many of aromatic com-

pounds: 12 g. of picric acid were dissolved in 100 cc. of the fraction, warmed. After one day the fraction became filled with yellow crystals.

**CHEMICAL COMPOSITION**—The smoky constituent was treated with acetic anhydride and a comparatively insoluble portion separated from it. After repeating this operation several times a pure smoky constituent was obtained which yielded no non-nitrated portion on nitration. Similarly a concentrated non-smoky constituent was obtained which yielded 10 per cent nitrated portion on nitration. Combustions of the two constituents gave the following results:

Constituent	Per cent C	Per cent H	Ratio of C to H
Pure smoky.....	88.98	10.75	1:1.44
Concentrated non-smoky.....	85.43	14.34	1:2.00

The former is rich in carbon atoms. Being a mixture of compounds boiling between 150° C. and 250° C., its molecular formula can not be determined by the above composition, but it is supposed from the boiling point that the number of carbon atoms is between 9 and 15. If these numbers are applied to  $C_9H_{14.44}$ , it becomes  $C_9H_{12.96}$ — $C_{15}H_{21.6}$ , i. e.,  $C_nH_{2n-5.04}$ — $C_nH_{2n-8.4}$ . These formulas are richer in carbon atoms than paraffins, naphthenes, or olefins: they correspond to aromatic compounds. The above formulas indicate that the non-smoky constituent is composed of paraffins or naphthenes.

From the above described experiments it was concluded that the nitrated portion consisted of aromatic compounds, and about 42 per cent by volume of the kerosene fraction was nitrifiable. On that account the kerosene fraction was richer in carbon atoms than an ordinary kerosene oil from another origin, and burned incompletely in an ordinary lamp.

#### IV—REFINING THE KEROSENE OIL

In the previous paragraph it was concluded that the smoky burning of this oil was due to the presence of large amounts of aromatic compounds. Though this smoky constituent could be separated by acetic anhydride as described in Section II, this method could not be used economically for the commercial refining of burning oil, on account of the high price of acetic anhydride. Accordingly, another refining method for this oil was sought. On ordinary sulfuric acid treatment, the quantity of the acid and temperature and duration of the treatment were changed variously.

**EXPERIMENT 3**—100 cc. of the kerosene fraction boiling between 150° C. and 250° C. were mixed with 100 cc. of concentrated sulfuric acid (sp. gr. 1.84), stirred with an agitator connected to a water turbine. In the course of time the acid layer absorbed some portion of the oil, and increased gradually in quantity. After agitating for twenty hours, the oil layer was separated, washed well with water and a dilute alkali solution. The specific gravity of the oil decreased from 0.825 to 0.791, and the oil burned brilliantly. Next the kerosene fraction was treated with smaller quantities of the acid, and the results obtained follow.

The nitrifiable portion in the following table was determined by the method described above.

Treatment of kerosene agitated	Sp. gr. of treated oil at 30° C.	Vol. of acid layer formed	Nitrifiable portion in treated oil at 20° C.	Refractive index of oil at 20° C.	CHARACTER OF FLAME
with H <sub>2</sub> SO <sub>4</sub> for hrs.			Per cent		
100 20	0.825		42.0	1.4705	Very smoky
75 20	0.797	125.4	12.0	1.4468	Very good
50 20	0.797	98.0	15.0		Very good
25 20	0.803	67.0	19.0		Good
10 20	0.821	44.0	23.0		Not smoky but easily undulated
25 5	0.808	43.0	23.0	1.4577	Good
10 5	0.821	17.0	35.0		Not smoky but easily undulated
Repeated last treatment			28.0	1.4682	Good

From the above table it was evident that there was no difference between the reactions for 20 hours and 5 hours, and that on the reciprocal proportion of the acid used, specific gravities, refractive indices and nitrifiable portions of the treated oil gradually decrease.

It was also seen that when less sulfuric acid than 25 cc. was used, the nitrifiable portion in the treated oil decreased in the ratio of about 7 cc. for 10 cc. of sulfuric acid used, and in the same ratio the acid layer absorbed the oil. When more sulfuric acid was used, the ratio decreased.

**EXPERIMENT 4**—100 cc. of the kerosene fraction were introduced into a flask provided with a reflux condenser, and mixed with various quantities of concentrated sulfuric acid (sp. gr. 1.84). The mixture, warmed on a water bath, was agitated for five hours by a dry air current. After treatment, the oil was separated from the acid layer, and washed. The oils thus obtained were yellow in color; their quantities are tabulated below:

Sulfuric acid used	Acid layer separated	Nitrifiable portion in oil	CHARACTER OF FLAME
cc.	cc.	Per cent	
Original oil	..	42	Very smoky
20	44	18	Very good
15	33	24	Very good
10	22	30	Very good
5	11	36	Good
3	7	38	Not smoky but easily undulated

From the above it was clear that sulfuric acid acts more effectively at 100° C. than at ordinary temperature. The increase of acid layer by the treatment was proportional to the quantity of sulfuric acid used. For 10 cc. of sulfuric acid used, the increase of acid layer was 12 cc., and the decrease of nitrifiable portion in the treated oil was also 12 cc. From this result, it was concluded that the nitrifiable portion by which the kerosene fraction was contaminated, was absorbed by the acid in almost definite proportions. The sulfuric acid acted upon nitrifiable oil in the kerosene fraction 1.7 (12/7) times more effectively at 100° C. than at ordinary temperature.

If the kerosene fraction was treated by sulfuric acid at 100° C. for five hours, a usable oil was obtained by 5 per cent of sulfuric acid, and the more sulfuric acid used, the better the oil obtained.

Afterwards two samples of new crude petroleum were obtained and tested as to solubility in acetic anhydride: the nitrifiable portions were determined in them by the method described in this paper and it was found that the above methods were applicable for the testing of oil for the presence of compounds rich in carbon.



# **THERMAL REACTIONS IN CARBURETING WATER GAS** **PART II—EXPERIMENTAL**

By M. C. WHITAKER AND W. F. RITTMAN

Received April 13, 1914

In the design of an experimental apparatus for cracking oil in accordance with the theory set forth in *THIS JOURNAL*, 6, 383, it is necessary to provide accurate control over the three variables: temperature, pressure, and concentration. The plan of research has been: (1) To keep pressure and concentration constant until the effect of changing temperature is understood; (2) to keep the temperature constant and change the total pressure on the system; (3) to hold both temperature and pressure constant and crack the oil in the presence of other gases in order to vary the concentrations.

Considerable time was spent in designing and building an apparatus which would be stable, durable, easy of access and replaceable in all its parts, as well

brand wrought iron pipe, 32 in. long. For a length of 18 in. the pipe is wrapped with No. 15 Nichrome resistance wire, seven turns to the inch. Between the wrought iron pipe and resistance wire five layers of asbestos paper serve as insulation. In series with the nichrome wire of the furnace is a large rheostat, with graduated steps between  $2\frac{1}{2}$  and 9 amperes. An incandescent tell-tale lamp is connected across the binding posts of the furnace, to indicate when the current is on as well as to give a rough idea of the wattage in use. Both voltmeter and ammeter are connected in the circuit. (See Fig. I.)

The nichrome wire windings are enclosed in a five-inch insulation of magnesia-asbestos pipe covering to minimize radiation. A  $\frac{3}{4}$  in. wrought iron pipe is welded at right angles into the  $1\frac{1}{2}$  in. wrought iron furnace body to serve as a container for the pyrometer point. This side tube is likewise insulated with asbestos and is fitted with a stuffing box surrounding the

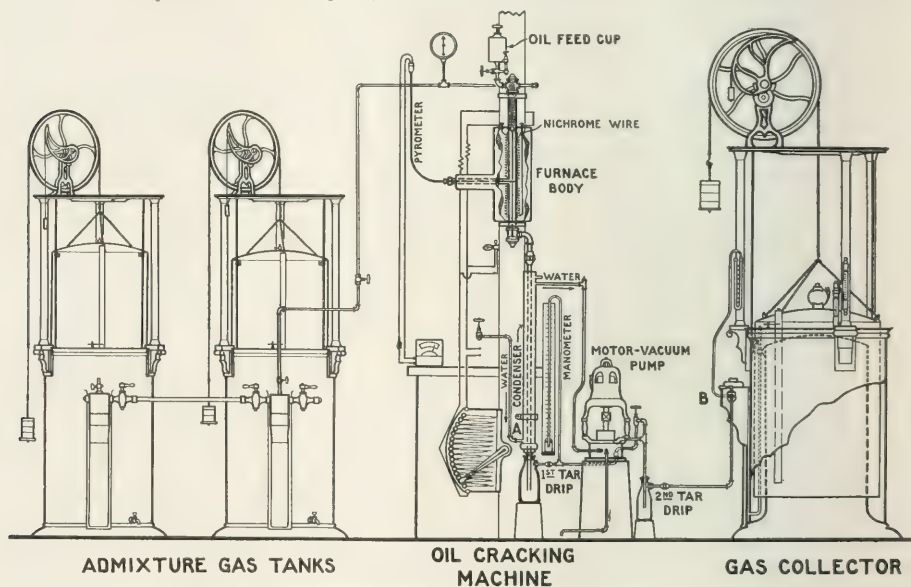


FIG. 1.—APPARATUS FOR OIL CRACKING AND GAS MAKING

as under complete control with respect to temperature, pressure and concentration. The machine was further designed to be of such dimensions and capacity as would indicate results which might be expected in the commercial application of the principles involved. In its completed form the apparatus covers a floor space sixteen feet by four feet and the oil feed cup at the top of the machine is nine feet from the floor. With this equipment it is possible to maintain any temperature up to  $1000^{\circ}$  C. within five degrees, and any pressure ranging from one-thirtieth of one atmosphere absolute to three atmospheres absolute.

## **FURNACE BODY**

The furnace body is made from  $1\frac{1}{2}$  in. "Reading"

pyrometer rod. With this side tube it is possible to keep the pyrometer point directly in the furnace body at all times. The pyrometer couple is of the iron-nickel type connected with a millivoltmeter calibrated in degrees Centigrade.

After continued use at the higher temperatures the furnace body warps or the nichrome wire burns out. Duplicates for all parts are kept on hand, and the apparatus is so designed that any part may be replaced within a few minutes.

In order to vaporize the oil before it reaches the cracking zone, the upper part of the furnace tube is filled with  $\frac{5}{8}$  in. steel balls. These are held in place by a thin post which runs vertically through the furnace supporting a perforated plate. The vertical rod

is bent to permit the centering required for the pyrometer. The object of the steel balls is to spread the oil in thin films and facilitate vaporization, but not to serve as cracking surface; in order to accomplish this they are kept at a safe height above the cracking zone. Lowering them into the cracking zone has a marked influence on the products obtained from the cracking process. The furnace, together with condenser, oil feed, pressure gauge and admixture gas-inlet pipe are vertically supported by iron clamps attached to an upright 3 in.  $\times$  6 in. yellow pine timber. The assembled apparatus was tested at 100 lbs. hydraulic pressure.

#### OIL FEED

A Powell sight feed oil cup of one quart capacity is joined by a  $\frac{3}{4}$  in. elbow and nipple to a  $1\frac{1}{2} \times 1\frac{1}{2} \times \frac{3}{4} \times \frac{3}{4}$  in. cross which forms the upper end of the furnace body. The pressure in the oil cup is equalized through a small internal pipe which communicates with the furnace body below the point of oil discharge. As a result of this equalizing tube, regardless of whether the apparatus is under increased or reduced pressure, the oil supply is always under a supply pressure equal to its own head. As this head decreases the rate of flow may be regulated by the needle valve controlling the feed inlet. The rate of supply may be determined by counting the drops for a given time.

#### PRESSURE GAUGES

For all vacuum work the apparatus is connected with a mercury manometer calibrated in inches. A mechanical vacuum gauge is also placed at the top of the apparatus to indicate a free path in the cracking tube. In the course of the experiments under certain conditions, sufficient carbon was deposited to clog up the apparatus and show a considerable difference in the pressure between the two gauges. Such a condition, however, is limited to experiments involving high temperatures and pressures (atmospheric or greater), where the deposition of carbon is at its maximum. There is never any clogging under reduced pressures. For pressure work, the mercury column is disconnected and a mechanical pressure gauge is substituted.

#### CONDENSER

At the lower end, the generating tube or furnace body discharges through a Liebig type condenser into a tar drip for the collection of liquid condensates. The cooling water enters at the bottom of the condenser and on leaving continues through the jacket of the vacuum pump. The condenser pipe is offset from the furnace body rather than placed directly under it so that the furnace may be cleaned by simply removing the lower plug and withdrawing the contents. It is thus possible to remove and weigh the deposited carbon from the furnace body after each run.

#### TAR DRIPS

For vacuum work the tar drips are of glass, as this facilitates observation of the gas, as well as the nature and the rate of tar formation. In vacuum work it was soon found that the lighter condensates would con-

tinue through the vacuum pump because of the low pressure in the first tar drip. To collect the liquids drawn through, a second tar drip was placed beyond the vacuum pump. Upon reaching the second drip these lighter hydrocarbons condense, as the pressure is then approximately atmospheric. When working under one-thirtieth of an atmosphere it was found that only a small percentage of the hydrocarbons would collect in the first tar drip. For pressure work a steel tar collector was substituted.

#### VACUUM PUMP

Vacuum in the system is maintained by a May-Nelson two-ring vacuum pump. By means of a bypass connection joining the outlet and inlet of the pump, it is possible to regulate the valve so as to maintain any desired vacuum down to one-thirtieth of an atmosphere.

#### CONNECTION FOR PRESSURE WORK

The vacuum pump is mounted on a movable concrete foundation and by disconnecting a few couplings the vacuum attachments may be removed. For pressure work there is substituted an all metal tar collector, connecting pipe, and release pressure valve, as shown in Fig. II. The apparatus may be changed from vacuum to pressure, or *vice versa*, in twenty minutes. When working under pressure, the gas

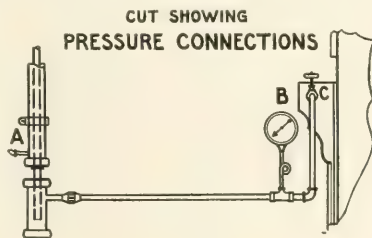


FIG. II

generated in the furnace body creates its own pressure. This pressure is controlled by an ordinary release valve placed at the inlet to the gas collector. By regulating the release of this valve, the apparatus may be set to work under any pressure from atmospheric to 30 lbs. per square inch above atmospheric, which seemed to be the upper safe working limit of the furnace under the conditions of operation. A pressure gauge is placed in the discharge line and used as a check on the pressure gauge near the oil feed.

#### GAS COLLECTOR AND ADMIXTURE GAS TANKS

The gas generated is collected in a 12 cu. ft. capacity gas holder, made by the American Meter Company. The tank is graduated in tenths of a cubic foot. By multiplying the number of cubic feet by 28.32 the volume is reported in liters. To avoid relying upon natural diffusion for mixing the gases, the bell of the holder is fitted with an internal mechanical stirrer directly connected through a stuffing box to an electric motor located on top of the bell. Perfect mixing of the gases may be attained in two minutes with this

equipment whereas natural diffusion would require from one to two hours.

The equipment also contains two 6 cu. ft. capacity admixture tanks of the same design as the large holder. These serve as gas supply tanks when cracking oil in the presence of other gases such as  $H_2$ , CO, or mixtures of the two. A  $1/4$  in. steel pipe, fitted with needle control valves, connects these two tanks with the inlet end of the furnace body. The piping is so arranged as to connect any two of the three tanks.

#### METHOD OF MAKING A RUN

When the apparatus is operated under vacuum the furnace body is first heated by the resistance coils to the desired temperature for cracking the oil into fixed gases. The oil is permitted to enter the upper part of the generating tube where it spreads over the steel balls and is vaporized. In the meantime, the vacuum pump has been set in operation and draws the oil vapors downward into the cracking zone of the furnace body, whereupon these vapors are immediately cracked into fixed gases and other products. These products, before opportunity is offered for polymerization or decomposition of the hydrocarbon gases, are withdrawn by the vacuum pump from the cracking zone and their place is taken by a quantity of oil vapor from the vaporizing zone above. In this manner the hydrocarbon gases are withdrawn continuously and as quickly as they form. After they pass through the condenser and receiver for the removal of the condensable vapors, they are forwarded by way of the pump to the gas holder.

TABLE I TYPICAL VACUUM RUN RECORD

Time	Room temperature, 15° C.		Barometer, 756 mm.	
	Temp. ° C.	Vacuum Inches	Oil feed Drops in 10 sec.	Cu. ft. gas observed
11 43	900	29.00	.	
12.00	903	28.50	.24	
12.15	905	28.00	.26	2.16
12.30	895	28.75	.23	3.01
12.45	895	28.75	.21	3.76
1.00	895	28.50	.24	4.86
1.30	895	28.50	.26	6.86
1.45	895	28.50	.25	7.76
2.00	895	28.75	.17	8.36
2.07	Run ended			8.75

Corrected to standard conditions as follows:

$$8.75 \times \frac{273}{288} \times \frac{756}{760} \times 28.32 = 234 \text{ liters.}$$

#### ANALYSIS OF PRODUCTS FROM TABLE I GAS ANALYSIS

	Per cent by vol.	Liters at std. cond
CO	0.1	
H <sub>2</sub>	52.1	122.0
O <sub>2</sub>	0.9	
CO <sub>2</sub>	0.4	
CH <sub>4</sub>	1.0	56.0
C <sub>2</sub> H <sub>6</sub>	1.3	3.0
H <sub>2</sub>	1.5	40.0
N <sub>2</sub> difference	3.9	
	100.0	

Carbon, 3 grams

Tar, 60 cc. Sp. gr. 20. Bc

#### GAS SAMPLING AND ANALYSIS

After the gas in the holder is thoroughly mixed by the mechanical stirrer, three or four sampling

tubes are filled for analysis. As a guide for all methods of gas analysis, Dennis' 1913 edition of "Gas Analysis," using the Hempel equipment, is followed. To determine the hydrogen in a mixture of hydrogen, methane and ethane, Hempel's fractional combustion method<sup>1</sup> is used. All analyses are made in duplicate.

#### DATA OBTAINED FROM A RUN

In this work all conditions outside of temperature, pressure, and concentration were maintained as uniform as possible. Four hundred cc. of oil were used per run, fed at the rate of about 3 cc. per minute. The oil used is technically known as "150° (F.) water white oil;" its specific gravity at 15° C. is 0.7984; boiling point between 150° and 290° C. Oil from the same tank was used throughout the experiments. All runs were made in duplicate.

#### EFFECT OF TEMPERATURE CHANGES

The experimental data on changes in temperature in the cracking of the oil, with pressure and concentration maintained constant, agree with the data recorded in the literature from the experiments by Haber,<sup>2</sup> Hempel,<sup>3</sup> Ross and Leather,<sup>4</sup> Lewes,<sup>5</sup> Fulweiler,<sup>6</sup> and others. It is difficult to make accurate comparisons of two experiments conducted in different apparatus on account of the great variety of conditions involved. Subjecting a gas to a temperature of 900° C. for five seconds is quite different from subjecting it to the same temperature for five minutes.<sup>7</sup> Leading the gases through a  $1/8$  in. pipe heated to 900° C. would give different results from those obtained by leading the same gases through a 2 in. pipe heated to 900° C. While the difference due to experimental apparatus would not be so great as the examples cited, there is sufficient difference to affect the value of direct comparison.

TABLE II

Oil used, 400 cc			
Temp. ° C.	Press.	Gas liters Standard conditions	Carbon Tar
		Grams	Cc
650	atmos.	135	3
750	atmos.	206	18
900	atmos.	382	115

#### Analysis of Gas from Table II

Temp. ° C.	C <sub>2</sub> H <sub>6</sub> Per cent	CH <sub>4</sub> Per cent	H <sub>2</sub> Per cent	H <sub>2</sub> Per cent
650	10.2	33.7	9.1	43.6
750	4.9	41.1	19.2	30.6
900	None	46.7	38.6	13.1

However, the general results obtained at different temperatures by different experimenters are comparable. As the temperature increases, the quantity of valuable gas from a given amount of oil increases to a maximum, after which the gaseous hydrocarbons rapidly decrease and the deposited carbon increases.

<sup>1</sup> *Z. anorg. Chem.*, **1912**, 1841.

<sup>2</sup> *Jour. f. Gasb.*, **1896**, 799, 813, 830.

<sup>3</sup> *Ibid.*, **1910**, 53.

<sup>4</sup> *Journal of Gas Lighting*, **1906**, 825.

<sup>5</sup> *Jour. Soc. Chem. Ind.*, **1892**, 584.

<sup>6</sup> Rogers', *Industrial Chemistry*.

<sup>7</sup> Lewes, *Proceedings of Royal Soc.*, **1894**, 90; W. A. Bone, *Jour. f. Gasb.*, **1908**, 803; Bone and Coward, *Jour. Chem. Soc.*, **1908**, 1197.



The quantity of tar decreases, but this is due to a dissociation of the hydrocarbons and cannot be construed favorably. Upon subjecting the oil to temperatures of 650°, 750° and 900° C., under atmospheric pressure, the results are as shown in Table II.

#### EFFECT OF INCREASED PRESSURE ON GASEOUS REACTIONS

It seems reasonable to expect that a high pressure

expand to many volumes of gas than under reduced pressure.

In the system



one would expect that the application of high pressures would increase the difficulty of generating gas, and after the gas is generated it would make easier

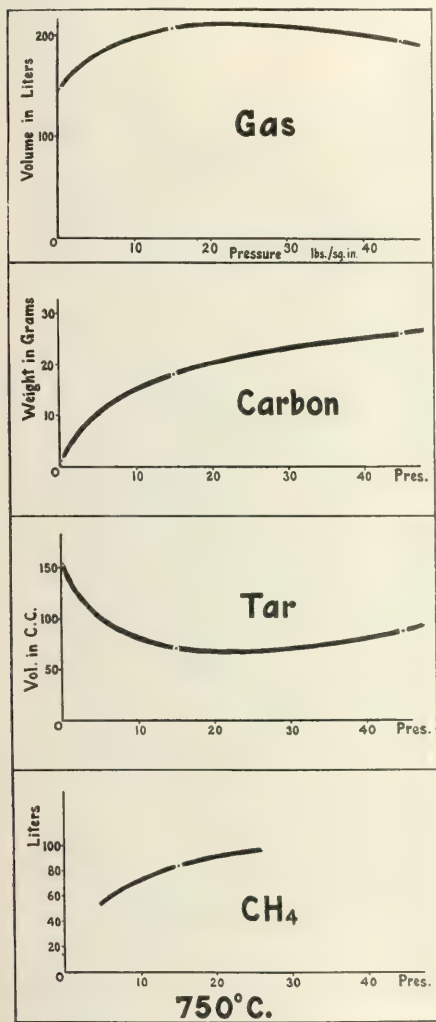


FIG. III.—VARIATIONS IN YIELDS OF PRODUCTS AT 750° C., UNDER VARYING PRESSURES. (TABLES II, III, IV AND VI)

will assist materially in condensing three volumes of acetylene into one volume of benzene:  $3\text{C}_2\text{H}_2 \rightleftharpoons \text{C}_6\text{H}_6$ . On the other hand, it seems reasonable to expect that, under a high pressure, it will be considerably more difficult for one volume of oil vapor to break up or

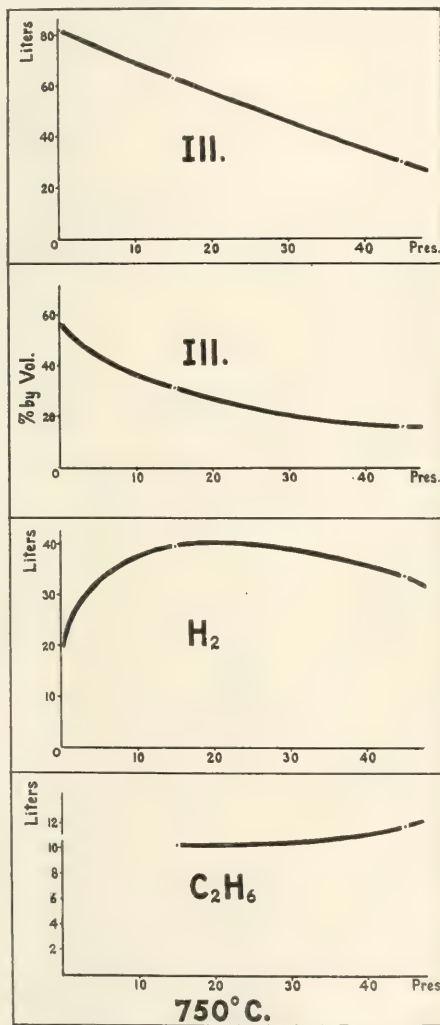


FIG. IV.—VARIATIONS IN YIELDS OF PRODUCTS AT 750° C., UNDER VARYING PRESSURES. (TABLES II, III, IV AND VI)

the condensation reactions which proceed to the tar stage. Since the unsaturated hydrocarbons, ethylene and acetylene, polymerize most readily, increased pressure should preferably condense them with the formation of tar compounds. In addition to the direct

TABLE III  
Oil used, 400 cc.

Temp. °C.	Pressure Absolute Lbs.	Gas Liters	Carbon Grams	Tar Cc
650	45	145	8	134
750	45	194	26	87
900	45	310	165	9

influence of pressure, it may be assumed that when working under increased pressure the gaseous hydro-

Analysis of Gas from Table III

Temp. °C.	C <sub>2</sub> H <sub>4</sub> Per cent	CH <sub>4</sub> Per cent	H <sub>2</sub> Per cent	III Per cent
650	11.5	45.1	9.3	30.5
750	6.1	56.6	17.5	15.5
900	None	41.6	50.0	5.0

The yields of gaseous hydrocarbons are lower than those shown in Table II, which were obtained at the same temperatures, and likewise the maximum yield

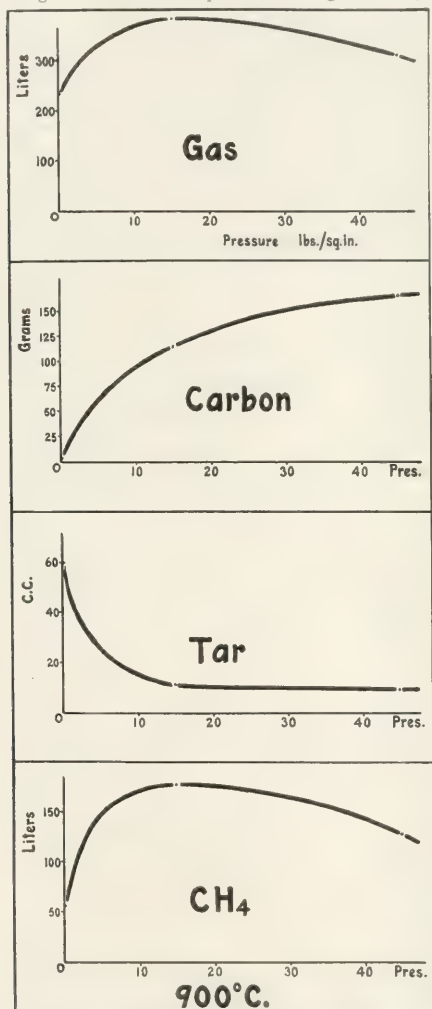


FIG. V.—VARIATIONS IN YIELDS OF PRODUCTS AT 900°C. UNDER VARYING PRESSURES. (TABLES II, III, IV AND VI)

carbons are subjected to the influence of heat for a longer time, which further tends towards the formation of heavy condensation products at the expense of the illuminants. The series of experimental results in Table III appears to justify these conclusions.

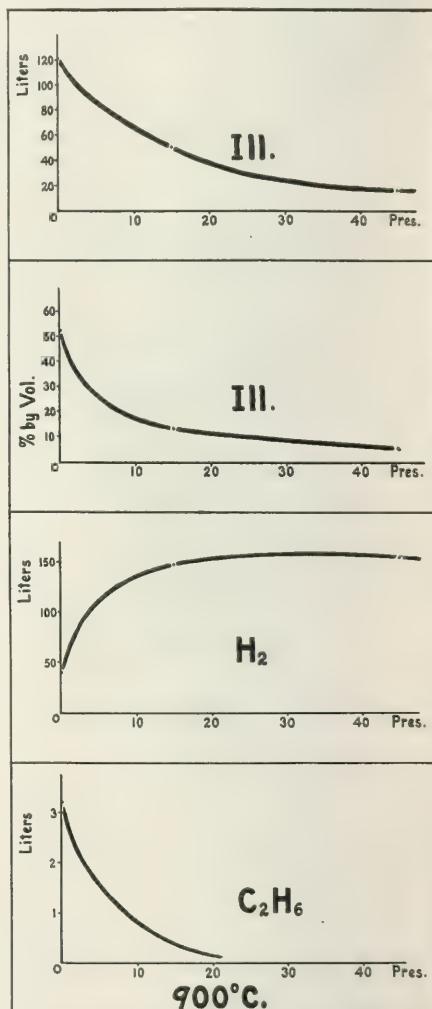


FIG. VI.—VARIATIONS IN YIELDS OF PRODUCTS AT 900°C. UNDER VARYING PRESSURES. (TABLES II, III, IV AND VI)

is lower than the maximum obtained under atmospheric pressure.

#### EFFECT OF DIMINISHED PRESSURE ON GASEOUS REACTIONS

By referring to the OIL-GAS-TAR system cited

TABLE IV—Oil used, 400 cc

Temp ° C.	Pressure Absolute	Gas Liters	Carbon Grams	Tar Cc
750	1/20 to 1/30 atmos.	146	1	153
850	1/20 to 1/30 atmos.	211	3	100
900	1/20 to 1/30 atmos.	234	3	60
950	1/20 to 1/30 atmos.	235	12	58

Analysis of Gas from Table IV

Temp. ° C.	C <sub>2</sub> H <sub>4</sub> Per cent	CH <sub>4</sub> Per cent	H <sub>2</sub> Per cent	Ill Per cent
750	.	.	12.5	56.1
850	3.4	20.5	15.6	52.9
900	1.3	24.0	17.3	52.1
950	Trace	27.0	20.8	46.9

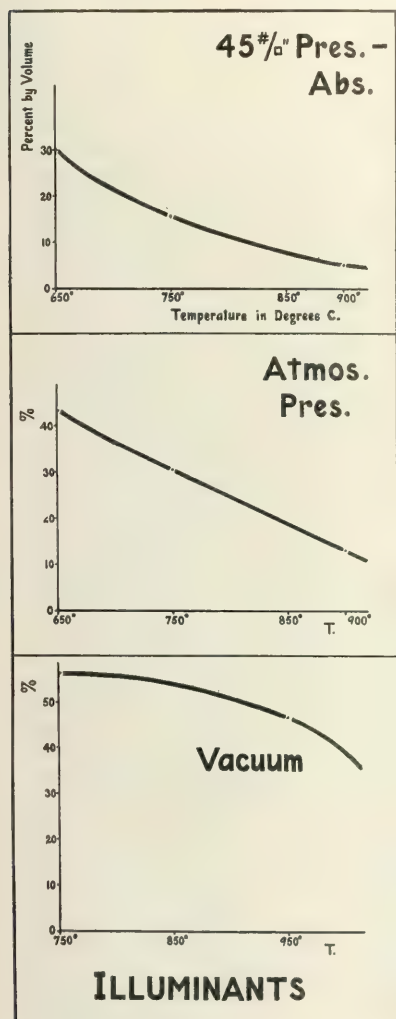


FIG. VII—PERCENTAGES OF ILLUMINANTS UNDER VARYING TEMPERATURES AND PRESSURES. COMPILED FROM TABLES II, III AND IV

above, it becomes evident that a high vacuum would favor the increase in volume due to cracking the oil into gas and at the same time withdraw the gas from the heat zone before it could form tar. The effects of this reduced pressure can best be observed from the results of the experiments in Table IV.

This striking difference in end products due to di-

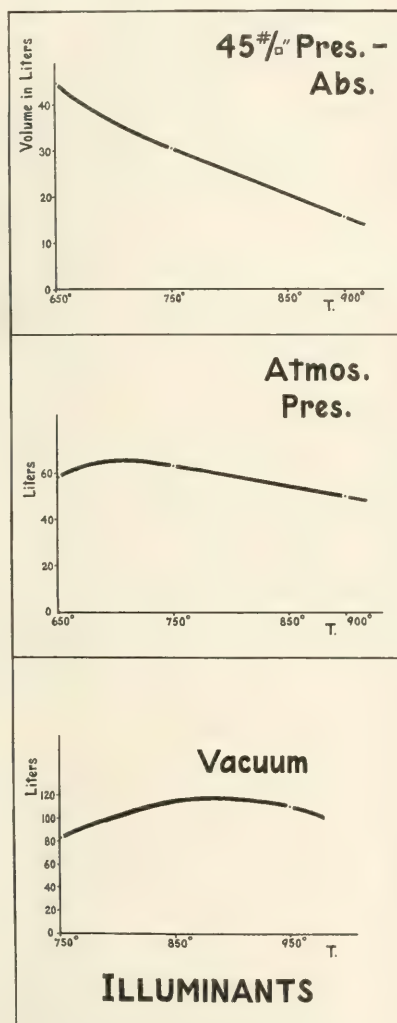


FIG. VIII—LITERS OF ILLUMINANTS UNDER VARYING TEMPERATURES AND PRESSURES. COMPILED FROM TABLE VI

minished pressure seems to have been overlooked, perhaps because for the first few pounds per square inch vacuum the increase is not marked.

#### INFLUENCE OF CONCENTRATION CHANGES ON GASEOUS REACTIONS

The present investigation has merely opened this



field. It has been established that oil cracked in an atmosphere of a gas, such as hydrogen, which reacts chemically with the end products of the cracking process, will yield products which are not analogous to those resulting from a physical mixture of the two gases. Not only does the mere presence of the admixed gas influence the end products, but as is to be expected from the theoretical consideration, the quantity of the admixed gas is influential.

To study the various gases and their quantitative relation will require much further experimental work. The results of preliminary study indicate that there is a vital relationship between the resulting gases in a cracking process and the atmosphere in which the oil is cracked. This relationship is likely to be of commercial significance in practical water gas carburization. The quantity of CO and H<sub>2</sub> admixed per gallon of oil cracked is an important factor, just as the temperature and the pressure have been shown to be important factors. Jones,<sup>1</sup> in his improved all oil water gas process, recognizes the importance of adding an "active gas" to the cracking zone, but considers the effect of the presence of the admixed gas to be catalytic. Hempel<sup>2</sup> found that by cracking oil in the presence of hydrogen not only did none of the hydrogen split off from the hydrocarbons, but part of the admixed hydrogen actually combined for the formation and preservation of hydrocarbons. On the other hand, on the basis of a single experiment reported, he maintains that the presence of CO in the cracking zone is similar to the presence of a neutral gas and is without material influence on the end products obtained from the oil. As to the hydrogen, the results of this research agree with the observations of both Hempel and Jones. The quantity and quality of gas per cc. of oil increase, and qualitative results show that the tar and deposited carbon decrease.

TABLE V

Temp ° C.	Pressure Absolute Lbs.	H <sub>2</sub> admixed. L.	Liters			Shrinkage in H <sub>2</sub>	
			C <sub>2</sub> H <sub>6</sub>	CH <sub>4</sub>	Ill	H <sub>2</sub>	Liters
750	15.0	358	15.4	125.0	70.6	308	50
800	15.0	412	18.0	116.0	83.2	335	77
750	0.75	400	9.5	52.0	112.0	381	19
810	0.75	413		86.5	140.0	378	35
860	0.75	388		99.5	133.0	350	38
900	0.75	292		92.0	120.0	272	20
960	0.75	382		95.0	113.0	348	34

From these results it appears that a greater percentage of the admixed hydrogen enters into combination to form saturated hydrocarbons when the cracking process is carried out under atmospheric pressure, than is the case under greatly reduced pressure. The percentage increase in yield of the illuminants when the cracking process is carried out under reduced pressure in the presence of hydrogen is about as great, however, as is the percentage increase in illuminants when the reaction is carried out under atmospheric pressure.

<sup>1</sup> *The Gas Age*, 1913, p. 369, *American Gas Light Journal*, 1913, p. 272; *Gas World*, 1913, 916.

<sup>2</sup> *Jour. Gas*, 1910, p. 53, et al.

#### INFLUENCE OF TEMPERATURE, PRESSURE AND CONCENTRATION CHANGES ON COMPOSITION OF RESULTANT TAR

If changing temperature and pressure have a marked influence on the quantity and quality of gaseous hydrocarbons obtained from cracking petroleum oil, one should expect simultaneous changes in the condensable hydrocarbons, which differ from the permanent gaseous hydrocarbons only in that they are liquid or solid at ordinary temperatures. There should be equilibrium between all hydrocarbons of a series at the high temperatures prevailing in the furnace where practically all the hydrocarbons are gaseous. That the end products should contain ethylene and then suddenly jump to hexene is not to be expected, any more than that the hydrocarbons in coal tar would jump from benzene to naphthalene or anthracene. In industrial practice the "illuminants" are usually said to consist of 75 per cent ethylene and 25 per cent benzene vapor.

When the gas made by cracking oil in the apparatus under one-thirtieth of an atmosphere pressure absolute is passed over palladium in the presence of an excess of hydrogen, over 90 per cent of the illuminants are converted into saturated hydrocarbons, principally ethane, indicating that the illuminants contain but little, if any, benzene vapor. If the gas contains no benzene, it is only logical to believe that the condensable hydrocarbons contain no aromatic hydrocarbons. It is further found that the vacuum tar will combine with 1.82 sp. gr. sulfuric acid. It has a low specific gravity, and on permitting the higher boiling point fractions to stand, no naphthalene or anthracene separate out. Tars resulting from cracking oil in carbureting blue water gas under atmospheric pressure contain quantities of benzene, toluene and other aromatic hydrocarbons in sufficient amounts to be of commercial importance. In view of these facts, there is justification for the statement that tars which result from cracking petroleum under low pressures are different from those which result from cracking under atmospheric or higher pressure. Instead of benzene, toluene and other aromatic hydrocarbons, the vacuum tar contains members of the more unsaturated hydrocarbon series. The composition of these tars is now the subject of a further investigation.

#### SUMMARY

In the theoretical discussion on the influence of diminished pressure on oil gas manufacture, it was pointed out that one should expect an increase in the yield of gaseous hydrocarbons from a given amount of oil by reducing the pressure below atmospheric. This increase should reach a maximum as the absolute zero of pressure is approached. The correctness of this is shown by results recorded in Tables IV and VI. Not only are the gaseous hydrocarbon yields greatly increased, but the deposited carbon is practically eliminated, and there is much less gaseous hydrogen produced than in the product obtained at the same temperatures under higher pressure.

It was pointed out that increasing the total pressure under which the oil is cracked to several atmospheres

will decrease the gaseous hydrocarbon yields from a given amount of oil. Experimental results, shown in Table III, have proven this correct.

It was pointed out that varying the pressure on the system would enable one to better control the quantity and quality of "tar" obtained than at present where all tar is made under atmospheric pressure. Experimental results indicate considerable flexibility.

It has further been established that the end products resulting from cracking oil in an atmosphere of a gas, such as  $H_2$ , which reacts chemically with the end products of the cracking, are a function of both the composition and the quantity of the gas admixed, per Table V.

Experiments, Table IV, have proven that it is possible to "crack" oil at a temperature of 900° C. without depositing more carbon than 1 per cent by weight of the oil used.

TABLE VI—SUMMARY OF GAS TABLES

(All based on 400 cc. oil and calculated to 0° C., and 760 mm. pressure)

Temp. ° C.	Pressure sq. in.	Gas L.	Carbon G.	Tar Cc.	$C_2H_6$ L.	$CH_4$ L.	H. L.	III L.
Atmospheric Pressure Group (See Table II)								
650	15.0	135	3	163	13.8	45.5	12.1	88.8
750	15.0	206	18	80	10.15	84.5	39.6	63.0
900	15.0	382	115	11	Trace	178.1	148.2	50.0
High Pressure Group (See Table III)								
650	45.0	145	8	133	16.7	65.2	13.1	44.3
750	45.0	194	26	87	11.8	110.0	33.9	30.1
900	45.0	310	165	9	None	128.9	155.0	15.5
Low Pressure Group (See Tables I and IV)								
750	0.75	146	1	153	..	..	18.3	82.0
850	0.75	211	3	100	7.16	43.2	32.9	111.5
900	0.75	234	3	60	3.0	56.0	40.0	122.0
950	0.75	235	12	58	Trace	63.4	48.8	110.0
Admixed Gas Group (See Table V)								
		Hydrogen admixed L.		Hydrogen shrinkage L.				
750	15.0	358		50	15.4	125.0	308.0	70.6
800	15.0	412		77	18.0	116.0	335.0	83.2
750	1.0	400		19	9.5	52.0	381.0	112.0
810	1.0	413		35	..	86.5	378.0	140.0
860	1.0	388		38	..	99.5	350.0	133.0
900	1.0	292		20	..	92.0	272.0	120.0
950	1.0	382		34	..	95.0	348.0	113.0

Through a proper consideration of equilibrium and mass action conditions under various degrees of temperature and pressure, much can be expected in gaseous reactions. It soon becomes evident that the single stage method wherein endothermic and exothermic, expansion and contraction reactions are combined in a single apparatus, is open to question.

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#### NOTE ON A BLACK BAND IRON ORE FROM THE STEARNS COMPANY'S COAL MINES AND ON THE CALCIUM-MAGNESIUM RATIO IN KENTUCKY CARBONATE ORES<sup>1</sup>

By ALFRED M. PETER

In September, 1913, the Stearns Coal Company sent to this Experiment Station, for analysis, a sample of

<sup>1</sup> Presented at the regular meeting of the Lexington Section of the American Chemical Society, February 11, 1914.

iron ore found immediately over the coal in their mines at Stearns, McCreary County, Kentucky. The ore occurs in a layer of about 18 inches maximum thickness, resting on the coal, and is capable of being mined with the coal. It is seal-brown in color, has a horizontal lamination or banding with carbonaceous matter between the laminae, and breaks transversely to the laminae, giving a rather smooth surface. On account of its structure and the presence of carbonaceous matter, it is here classed as "Black Band" ore, though distinctly brown, not black, in color and containing much less carbonaceous matter than is usual in black band.

An analysis by Mr. J. S. McHargue follows:

ANALYSIS OF THE AIR-DRIED SAMPLE No. 43255

Specific gravity (18° 18°) 3.268	
Ferrous oxid.....	51.77 per cent
Ferric oxid.....	0.85
Alumina.....	0.60
Manganous oxid.....	0.51
Calcium oxid.....	1.94
Magnesium oxid.....	3.57
Phosphorus pentoxid.....	0.08
Sulfur.....	Trace
Silica.....	1.16
Organic matter.....	2.77
Carbon dioxide, etc., by difference.....	36.69
Total.....	100.00
Total iron.....	40.87
Total phosphorus.....	0.035

Treatment with carbon disulfide extracted an appreciable amount of brown, bituminous matter, the quantity of which was not determined. The figure for organic matter was obtained by digesting a portion of the ore in HCl, filtering on a Gooch filter, washing, drying at 100°, weighing and burning, the loss in weight being taken to represent organic matter.

PROBABLE COMBINATIONS, CALCULATED FROM ABOVE ANALYSIS

Ferrous carbonate.....	83.50 per cent
Ferric oxid.....	0.85
Alumina.....	0.60
Manganous carbonate.....	1.29
Calcium carbonate.....	3.30
Magnesium carbonate.....	7.49
Tricalcium phosphate.....	0.17
Sulfate.....	Trace
Silica.....	1.16
Organic matter.....	2.77
Total.....	101.13

The analysis shows that this is quite a pure iron ore, containing, however, considerable quantities of manganese, calcium and magnesium. A notable feature is that there is more than twice as much magnesium carbonate present as calcium carbonate. Calculating to molecular proportions and including the manganese in the comparison, gives 1  $MnCO_3$  : 2.94  $CaCO_3$  : 7.81  $MgCO_3$ , or, in round numbers 1 : 3 : 8. The ratio of calcium carbonate to magnesium carbonate is 1  $CaCO_3$  to 2.66  $MgCO_3$ . Of course this may be only a chance relation, but there is room to speculate why there is more magnesium carbonate than calcium carbonate. Has it a relation to the greater solubility of magnesium carbonate in carbonated water? Or is it because there was more magnesium than calcium in the original material from which this ore was formed? No answer is suggested, but a fact like this, in the hands of a well informed chemical geologist, might help to explain the process by which this kind of iron ore is formed.

To show that magnesium usually predominates over calcium in the ferrous carbonate ores of Kentucky, all the analyses of such ores made for the first Kentucky

Geological Survey, 1856 to 1860, by Dr. Robert Peter, Chemist of the Survey, and published in the first four chemical reports, have been tabulated and compared.

The total number of samples analyzed was 71 from 20 counties, as follows: Bath 3, Bullitt 2, Butler 2, Carter 3, Crittenden 2, Edmondson 1, Estill 4, Greenup 26, Hancock 1, Hopkins 2, Laurel 4, Lincoln 1, Montgomery 1, Morgan 1, Muhlenberg 7, Nelson 2, Owsley 2, Powell 1, Pulaski 2, Whitley 3.

The geological formations represented were mainly the Coal Measures and the Devonian, with some from the "Sub-Carboniferous" of Owen, or Mississippian, and the Silurian.

The kinds of ore were various, including kidney ore, oolitic ore, massive kinds, black band, block ore and two samples which would better have been classed as ferruginous limestones. Probably most of the block ores should not have been included because, in these, the proportion of ferric oxid often exceeds that of ferrous carbonate.

The whole tabulation would occupy too much space here. Inspection of it brings out the following facts:

	No.
Analyses tabulated.....	71
Per cent. $MgCO_3$ exceeds per cent $CaCO_3$ .....	57
Per cent $MgCO_3$ equals per cent $CaCO_3$ .....	1
Per cent $MgCO_3$ is less than per cent $CaCO_3$ .....	13
Per cent Insoluble matter exceeds 10 per cent.....	45
Per cent $CaCO_3$ exceeds 10 per cent.....	2

These last two, of course, are included in the thirteen which contain more  $CaCO_3$  than  $MgCO_3$ . The large number containing more than 10 per cent insoluble matter shows that the collection includes many impure ores.

To gain a general idea of the composition of the samples in which the  $MgCO_3$  predominated over the  $CaCO_3$ , the 57 analyses of this class have been averaged, giving the figures in the following table, which includes also the extreme range of each constituent, all stated as per cent of the ore, dried at 100° C.:

COMPOSITION OF 57 SAMPLES	Average	Highest	Lowest
Ferrous carbonate, $FeCO_3$ .....	60.78	87.53	20.19
Ferric oxid, $Fe_2O_3$ .....	8.09	51.31	Trace
Alumina, $Al_2O_3$ .....	1.40	5.15	Trace
Calcium carbonate, $CaCO_3$ .....	2.71	7.25	Trace
Magnesium carbonate, $MgCO_3$ .....	5.92	13.99	0.83
Manganous carbonate, $MnCO_3$ .....	1.57	5.03	0.12
Insoluble residue.....	16.36	40.88	4.87
Combined $H_2O$ , bituminous matter and undetermined.....	3.17	...	...
Total.....	100.00		

It is seen that the proportion of magnesium carbonate is more than twice that of the calcium carbonate and that the proportion of manganous carbonate is the smaller of the three. Calculated to molecular proportions, the relation is 1  $MnCO_3$  : 2  $CaCO_3$  : 5.1  $MgCO_3$ . It is presumably only an accident, however, in such a calculation as this, that the molecular ratios are almost exactly whole numbers. The ratio of calcium carbonate to magnesium carbonate is 1  $CaCO_3$  to 2.55  $MgCO_3$ , which does not differ very far from the ratio found in the Stearns sample, *viz.*, 1  $CaCO_3$  to 2.66  $MgCO_3$ .

KENTUCKY AGRICULTURAL EXPERIMENT STATION  
LEXINGTON

## A NOTE ON THE UTILIZATION OF MUDS AND SCUMS FROM SUGAR REFINERIES

By R. F. GARDINER<sup>1</sup>  
Received March 3, 1914

A description of the muds and scums in the sugar refining processes can be found in most works on industrial chemistry. Thorp says that "these muds have been thrown away." The possibility of their utilization is now being seriously considered by some sugar producers, as is shown by recent correspondence between this laboratory and a prominent American sugar producer, who says: "The mud was thrown away for quite a time and now we are trying some experiments in drying the same for the phosphoric acid content."

Sample I was analyzed by the author; the nitrogen determination was kindly made by Mr. T. C. Prescott, of the Bureau of Chemistry. The analysis of Sample II, by Plicque, is cited because it also shows a considerable amount of water.<sup>2</sup>

TABLE I—SHOWING COMPOSITION OF MUD FROM A SUGAR MILL

Percentages	I Gardiner	II Plicque
$H_2O$ .....	67.32	52.70
Sugar.....	..	3.50
Nitrogenous matter.....	..	3.72
N.....	1.14	..
$K_2O$ .....	Trace	..
$PO_5$ .....	8.33	4.77
Lime, silica, iron, etc.....	..	26.07

In order to economically recover the valuable fertilizer elements, such as phosphoric acid and nitrogen, it will be necessary to find some satisfactory drying process, for which modern improvements in drying processes may offer ultimate success in the utilization of this potentially valuable fertilizer, now entirely lost.

BUREAU OF SOILS, DEPARTMENT OF AGRICULTURE  
WASHINGTON

## THE EFFECT OF HIGH TEMPERATURE ON YEAST

By C. B. COCHRAN<sup>1</sup> AND J. H. PERKINS<sup>2</sup>  
Received October 17, 1913

In the experiments recorded below, the yeast was added to 30 cc. of simple syrup in sterilized test tubes plugged with cotton, raised to the temperatures indicated and held there for the stated periods of time. The tubes were then placed in an incubator and kept at a temperature of about 31° C.

TUBE NO.	TEMP. ° C.	RESULTING FERMENTATION	
		Fleischmann's (b)	Magic (b)
SP. GR. OF SYRUP.	1 & 2	35	
AND TIME	1 & 2	40	
SP. GR., 1.125	1 & 2	45	
TIME, 5 min.	1	68	
	2	55	
	1 & 2	68	
	1 & 2	85	
SP. GR., 1.120.....	1, 2 & 3	48	
TIME, 30 min.....	1, 2 & 3	58	
SP. GR., 1.125	1, 2 & 3	65	
TIME, 30 min	1 & 2	70	
	3	70	
SP. GR., 1.126(a).....	1, 2 & 3	68	
TIME, 15 min.....	1, 2 & 3	72	

(a) In these tests the heat was applied after leaving the yeast in the syrup for 24 hours at a temperature of about 12° C.

(b) To each 30 cc. of syrup, 1/32 of a Fleischmann's or 1/16 of a Magic yeast cake was added.

PHILADELPHIA

<sup>1</sup> Scientist in Soil Laboratory Investigations.

<sup>2</sup> "Handbook for Planters and Refiners." Lock and Newlands Bros 1888, p. 489.

<sup>3</sup> Chemist for The Dairy and Food Department of Pennsylvania.

<sup>4</sup> Chief Chemist for The Charles E. Hires Company.



# PHYSICAL FACTORS WHICH INFLUENCE THE PERCENTAGE OF WET AND DRY GLUTEN IN WHEATEN FLOUR

By B. H. KEPNER

Received January 28, 1914.

The determination of crude wet and dry gluten is affected by so many physical conditions and is so unreliable that it has been almost wholly given up and the proteins are now determined in most laboratories by the more accurate Kjeldahl method. In exceptional cases when it is necessary to know the quality of the gluten, a qualitative determination is made. Arpin<sup>1</sup> recognizes the fact that there are numerous sources of error in the separation of the gluten. Jago<sup>2</sup> states that it is difficult and in many cases impossible to wash away the whole of the starch from flour without also washing away some of the more soluble parts of the gluten itself. In consequence, gluten determinations vary according to the thoroughness of washing and this differs in different hands. In spite of this assertion Jago still continues to attach importance to properly conducted gluten determinations, holding that the estimation of the quantity and quality of the wet gluten determines the quality of the resultant dough and bread. It has been my experience that, within the same grade, Straight, Patent, Bakers, etc., the higher the percentage and the better the quality of the wet gluten, the better baking results are obtained.

Because there is no standard method, each laboratory at present uses a method which is the most suitable for its use. Results are affected by the conditions and methods of manipulation by which they are obtained. They are not absolutely comparable from different laboratories because of the difference in physical conditions.

The following method we have adopted as being especially suitable for routine work: Weigh out thirty grams of flour in a large size coffee cup. Mix in enough water, about 17 cc., with a stiff bladed knife to make a dough of standard stiffness and continue the mixing until an absolutely uniform dough is obtained. Cover the dough with cold water, let stand one hour and then wash in a small stream of water at exactly 65° C. (over a sixty-mesh sieve) until nearly all the starch is washed away. Return gluten to cup, cover with cold water, let stand one-half hour longer and then wash until free from starch. The wash water should be clear and not milky. Cover the gluten with cold water until it is ready to weigh, then dry between the hands, wiping the excess of water on a clean, lint-free towel, place on white tared paper 2" X 2" and weigh. Place in oven at 170° C. to expand the gluten to a porous mass and bake it, then dry for twenty-four hours at 105° and again weigh.

It was found very difficult to check the determinations from day to day, hence, the effect of the different physical conditions were determined.

It is necessary to make an absolutely uniform dough of the water and flour, otherwise portions of flours are washed away like starch. Poorly mixed samples

give results which are 1 per cent lower in wet gluten and 0.2 to 0.5 per cent lower in dry gluten than a well mixed sample. The poorer the mixing, as a rule, the greater the loss.

If an excess of water is used for making the dough, the yield of wet gluten is increased from 1 to 3 per cent for the different grades, while insufficient water causes the percentage of gluten obtained to be lower. The percentage of dry gluten is not affected by this condition, showing that the higher or lower percentage of wet gluten is due wholly to water held by it.

If the doughs are kept covered with cold water before washing the percentage of wet gluten obtained in most cases increases with the length of time they are allowed to stand up to eight hours. They are kept cold in order to offset the influence of temperature and any fermentation. Arpin<sup>1</sup> shows that the wet gluten is increased 1.66 per cent by standing four hours, while the percentage of dry gluten remains unaltered. I find that very short patents and flours which have aged at least nine months are exceptions to this because there is only a very slight increase for even eight hours. Bakers and straight grades, when freshly ground, showed an increase of 1.50 to 3.50 per cent on standing eight hours. Low grades show an increase of only 0.3 per cent on standing one hour and a decrease of 2.5 per cent on standing eight hours. The low grades being high in natural ferments or bacteria suffer a loss by their action. The aged flours and short patents are unaffected because they contain less of these natural ferments than the freshly ground bakers and straight grades. All grades begin to decrease at the end of sixteen hours which would strengthen this supposition. The percentage of dry gluten remains the same up to sixteen hours on all flours with the exception of the low grade, which suffers a loss. After glutens are washed and allowed to stand for even twenty-four hours there is no change in weight. This shows that the increase or decrease in weight on standing eight hours before washing is due to some agency in the flour which is not included in the crude wet gluten.

The thoroughness of washing affects the results to a great degree. When glutens are washed in the usual manner, weighed, and then vigorously washed for five minutes more there is a loss of 5 per cent on the low grades, 3 to 4 per cent on the straights and bakers and 2.5 per cent on the high patents and old flours. There is also a loss of dry gluten. This loss varies with the manipulation and the vigorousness of the operation.

Arpin<sup>2</sup> states that the yield of gluten is increased 1.16 per cent with an increase of 10° in temperature of the water used for washing. We find that wet gluten increases 1.50 per cent for the same increase of temperature for all grades except the low grade, which shows a slight decrease. This can perhaps also be explained by the more active action of natural ferments caused by higher temperature. Arpin also found an increase of 1.16 per cent for the same range of temperature in the dry gluten. This point we have

<sup>1</sup> Jour. Soc. Chem. Ind., 1902, pp. 1417 and 1560.

<sup>2</sup> "Technology of Breadmaking," p. 296

<sup>1</sup> Jour. Soc. Chem. Ind., 1902, 1417 and 1560.

<sup>2</sup> Chem. Centr., 2 (1902), 1019 and 1347.

carefully investigated and at no time did we find an increase in the percentage of the dry gluten due to the increase in temperature.

In order to test the effect of temperature on the washed gluts they were allowed to stand twelve hours at 25° C., having been washed at 15° C. The gluts had become very sticky and hard to dry. The low grades all showed that fermentation had started. The low grades showed a marked decrease while the high grades showed only a slight decrease. This was also true of the dry gluts. Whatever agency causes the increase in weight, when the temperature of the wash water is higher than ordinary, is within the flour itself and is not contained in the wet gluten.

A higher percentage of gluten is obtained by washing in hard water than in soft. Hardy<sup>1</sup> is of the opinion that electrolytes or salts, which may be organic or inorganic, impress the property of tenacity and ductility on the gluten. Wood's<sup>2</sup> researches also prove that inorganic salts have a binding effect on gluten. All authorities agree that gluten cannot be washed from flour with pure distilled water because the gluten will not hold together. At first it forms a coherent mass but as soon as the salts, natural to the flour, are dissolved, the gluten scatters and cannot be collected again. If it be submerged in hard water when it first starts to scatter it forms again a coherent mass. There was an increase of 1 to 2 per cent in wet gluten for all grades when the gluts were washed in very hard water. There was only a slight change of about 0.25 per cent for the dry gluten at the most, showing that the hard water usually increased the water-absorbing capacity of the gluten.

#### CONCLUSIONS

It can readily be seen that conditions may be so different in various laboratories that the determinations of wet gluten are not comparable. Even for ordinary routine work, where comparative results alone are required, unless the utmost care is taken, the determination is unreliable. Since the percentage of dry gluten is very slightly affected by these same conditions it is more reliable.

1—Thoroughness of mixing affects both the per cent of wet and dry gluten.

2—An excess of water used in making the doughs increases, and insufficient water decreases the per cent of wet gluten. The dry gluten is the same.

3—The length of time the dough is allowed to stand increases the percentage of wet gluten up to eight hours. High patents, old flours and low grades are exceptions. The dry gluten remains unaltered except in the low grade where some fermentation has taken place.

4—Overwashing decreases the percentage of both the wet and dry gluten.

5—A larger per cent of wet gluten is obtained with warm wash water than with cold. The dry gluten is unaffected.

6—More wet gluten is obtained with "hard" wash

water than with soft. The dry gluten is slightly increased by the hard water.

WHEAT AND FLOUR TESTING LABORATORIES  
MAPLE LEAF MILLING CO. LTD.  
PORT COLBORNE, ONT.

#### THE DETERMINATION OF THE ACETYL NUMBER OF OILS, FATS, ETC.<sup>1</sup>

By EDWARD B. HOLLAND

Received January 13, 1914

#### INTRODUCTION

The various hydroxy compounds that occur in oils, fats and waxes form derivatives on heating with acetic anhydride, the acetyl radical displacing the hydrogen of the alcoholic hydroxyl groups. This property serves as the basis of analytical methods for the quantitative determination of these compounds. The proposed acetyl number indicates the milligrams of potassium hydroxide required for the saponification of the acetyl assimilated by one gram of an oil, fat or wax on acetylation.<sup>2</sup> On saponifying with alcoholic potash the acetyl is hydrolyzed to acetic acid and combines with the alkali to form potassium acetate. The results are expressed in terms of milligrams of potassium hydroxide to conform with the general practice in fat analysis. The compounds involved are mono- and dihydroxy acids and their glycerides, mono- and diglycerides and free alcohols.

#### USE OF THE TEST

In the examination of oils and fats a determination of acetyl number is necessary, in most instances, for a thorough understanding of the nature and quality of the product. Some of the hydroxy compounds are natural and others are the result of hydrolysis or of oxidation. Glycerides of hydroxy acids are a natural constituent of certain oils and fats although they do not appear to be very widely distributed in any considerable amount. Castor oil, composed largely of ricinolein, is a notable illustration. Hydroxy acids probably occur more frequently as the result of oxidation of unsaturated acids. Oleic acid has been shown repeatedly to be comparatively unstable. By the assimilation of oxygen and water it may be converted into dihydroxystearic acid, a saturated compound.

$C_{17}H_{33}COOH + H_2O + O = C_{17}H_{33}(OH)_2COOH$ . Whether the oxidation takes place in the glycerides or in the fatty acids after hydrolysis is uncertain, although the latter appears the more probable supposition.

Mono- and diglycerides result from the hydrolysis of triglycerides and free fatty acids condition their presence. The absence of free fatty acids in a commercial product, however, does not necessarily preclude the presence of mono- and diglycerides.

Solid alcohols of the cyclic series (sterols) occur in oils and fats both in combination as esters and as free

<sup>1</sup> The writer is pleased to acknowledge many suggestions and helpful criticisms by Dr. J. S. Chamberlain, Mr. F. W. Morse, Mr. J. C. Reed, and Mr. J. P. Buckley.

<sup>2</sup> Benedikt and Ulzer and Lewkowitsch report on the basis of the acetylated product.

<sup>1</sup> Supplement Jour., 4 (1910), 52; Jour. Board of Agric.

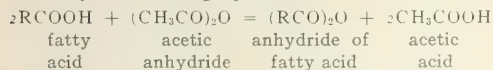
<sup>2</sup> Jour. Agric. Science, 2 (1907), 267.

alcohols.<sup>1</sup> The amount of cholesterol or phytosterol is generally small, often inappreciable, and is indicated approximately by the unsaponifiable matter which it characterizes. Alcohols of the ethane and other series, free and in combination, compose a considerable proportion of waxes.

Oils and fats, therefore, may contain glycerides of mono- and dihydroxy acids, possibly free hydroxy acids, mono- and diglycerides and free alcohols; and the insoluble acids, separated from the oils and fats, may contain mono- and dihydroxy acids and free alcohols. A portion, at least, of the free alcohols found in the insoluble acids probably occurred in the fat as esters. With the exclusion of the natural glycerides of hydroxy acids and a small amount of free alcohols, the acetyl number of many oils and fats may be deemed an index of quality and when considered in conjunction with the acid and iodine numbers, may serve to measure (more or less imperfectly to be sure) the amount of hydrolysis and of oxidation the product has undergone. To differentiate between products of hydrolysis and of oxidation, the acetyl number of the insoluble acids should also be determined.

#### EARLIER METHODS

The several analytical processes that have been offered are based on the same chemical reactions but differ in application and in details of procedure. The original method was devised by Benedikt and Ulzer<sup>2</sup> and applied to the insoluble acids. The acetyl number indicated the milligrams of potassium hydroxide required to neutralize the acetic acid obtained on saponifying one gram of acetylated insoluble fatty acids and was determined by the difference between the acid and saponification numbers of the acetylated acids (acetyl ether number). The actual procedure consisted in saponifying the acetylated acids after neutralizing in alcohol. Lewkowitsch<sup>3</sup> has shown, however, that the results so obtained were generally in excess of the true values due to the conversion of a part of the fatty acids, on heating with a large excess of acetic anhydride, into their anhydrides as illustrated by the following equation:



These fatty anhydrides are fairly stable compounds but may become hydrolyzed to some extent on washing with boiling water. Subsequent treatment with cold alcohol in the determination of the acetyl acid number will continue the hydrolysis although a portion is likely to remain unchanged, thereby yielding too low an acid number due to the inability of the anhydrides to combine with alkali. As complete hydrolysis occurs on saponification the acetyl (ether) number would be too high and even appear when none exists.

Lewkowitsch<sup>4</sup> proposed the acetylation of the nat-

<sup>1</sup> See numerous references: Abderhalden, "Physiological Chemistry," (1908); Hammarsten, *Ibid.* (1911); Leathes, "The Fats" (1910).

<sup>2</sup> *Monatsh. Chem.*, **8** (1887), 41-48.

<sup>3</sup> "Analysis of Oils, Fats and Waxes," **1** (1909), 344-5.

<sup>4</sup> *Loc. cit.*, **1** (1909), 337-8.

ural product. In conformity thereto the acetyl number indicates the milligrams of potassium hydroxide required for the neutralization of the acetic acid obtained on saponifying one gram of an acetylated oil, fat or wax. This method requires the saponification of the acetylated fat and the determination of the resulting acetic acid by either a filtration or distillation process. The former process is an adaptation of the regular method for the direct determination of soluble acids, and the latter process is a modified Reichert-Meissl test with repeated distillation of the aqueous solution until the distillate is free from acids. The presence of natural soluble or volatile acids necessitates a similar treatment of the unacetylated fat in order to determine the amount of alkali assimilated by those acids for which proper corrections must be made to obtain the true acetyl number. The occurrence of the lower acids makes the determination a long and tedious operation.

#### PROPOSED METHOD

Analytical methods for the examination of oils and fats is a subject that has been given considerable study by the writer in connection with feeding experiments and other investigations made at the Massachusetts Agricultural Experiment Station. During the past few years the determination of acetyl number has received particular attention with a view of evolving a process that might be free from the objections cited for the Benedikt and Ulzer and Lewkowitsch methods. Believing that this object has been obtained in some measure, a report of progress is now offered in the hope that it may lead to further improvement.

The custom of reporting acetyl number on the basis of the acetylated product appears unwarranted. It is contrary to general practice in analytical work and is the exception in fat analysis. The definition<sup>5</sup> adopted places the acetyl number on a par with other tests and is as follows: The acetyl number indicates the milligrams of potassium hydroxide required for the saponification of the acetyl assimilated by one gram of an oil, fat or wax on acetylation.

#### METHOD IN DETAIL

The development of the method extended over a period of several years and finally resolved into an adaptation of several well known processes. For instance, ceresine is used to solidify the acetylated fat so that it may be washed by decantation as in the determination of insoluble acids. The saponification number of the acetylated fat is determined by the same process as that of the original fat and the difference measures the amount of acetyl that has been assimilated. The process may be appropriately described as a method of analogy.

The reagents employed in the determination are summarized so that their application may be clearly understood:

Acetic anhydride, Kahlbaum's.

Ceresine, pure white, filtered.

Alcohol, redistilled, free from acids and aldehydes.

Alcoholic potash, 50 cc. of a saturated solution of potassium

<sup>5</sup> The hydroxyl value of Twitchell is reported in a similar manner. *Jour. Amer. Chem. Soc.*, **29** 1907, 566-71.



hydroxide, free from carbonate, to 1000 cc. of alcohol. The solution should be allowed to stand at least 24 hours and filtered immediately before use.

$N/2$  hydrochloric acid.

Alkali blue (6B), 1 gram to 100 cc. of alcohol. The indicator should be digested in a stoppered bottle for several days at room temperature, with occasional shaking, and then filtered.

Phenolphthalein, 1 gram to 100 cc. of alcohol, neutralized.

After what has been said, the details of the method should be sufficiently evident as to require no further explanation.

Into a 300 cc. Erlenmeyer flask are brought 5 grams of fat together with 10 cc. of acetic anhydride. The flask is connected with a spiral or other form of reflux condenser and heated in a boiling water bath (immersed in the water) for from 1 to 1.5 hours. Longer heating yields higher results but is accompanied by partial decomposition of the fat with formation of aldehydes or other bodies that give a reddish color with caustic alkali. After acetylating, the flask is removed from the bath and sufficient ceresine added to form, with the fat, a solid disc when chilled in cold water. The amount of ceresine required will vary with the consistency of the product under examination. For butter fat 0.4 to 0.5 gram is ample, for softer fats and oils rather more, and for harder fats less. The flask is heated on the water bath and the contents rotated until the ceresine and acetylated fat form a homogeneous mixture. 150 cc. of boiling water are then poured carefully into the flask with as little disturbance of the fat layer as possible and the solution heated on the bath with occasional agitation to remove occluded acetic acid. The flask is immersed in cold water to solidify the ceresine fat, after which the solution is decanted through a dense, ether-extracted filter, care being taken not to break the insoluble cake. Another 150 cc. of boiling water are added, thoroughly agitated, heated as above, cooled and decanted, the process being repeated until the final filtrate gives a decided color with 2 or 3 drops of  $N/10$  alkali, using phenolphthalein as indicator (about 6 times). Prolonged washing is likely to cause slight dissociation of the acetylated product.

The filter and inverted flask containing the cake of ceresine-fat are allowed to drain in a cool place until practically dry. The small particles adhering to the filter are then scraped into the flask, and 50 cc. of alcoholic potash, accurately measured with a burette, 50 cc. of alcohol and several glass beads added. The flask is connected with a spiral or other form of reflux condenser and the solution boiled on a water bath until saponification is complete—about 60 minutes. The flask is placed in a water bath at 60° C. and the solution, after cooling to that temperature, titrated with  $N/2$  hydrochloric acid, using 1 cc. of alkali blue as indicator. Phenolphthalein may be employed, though less satisfactory for colored solutions. The alcoholic mixture is again brought to boil to free any alkali occluded in the ceresine and retitred, if necessary. Several blank determinations should be run with every series of tests under precisely similar conditions as to time and treatment except that the ceresine may be omitted. However, every lot of ceresine must be tested, should be free from soluble matter and not assimilate any alkali on saponification. The difference between the titration of the blank and that of the excess alkali in the test is the acid equivalent of the fat after acetylation, which should be calculated to milligrams of potassium hydroxide for 1 gram of fat.

1 cc. of  $N/2$  acid is equivalent to 28.054 milligrams of potassium hydroxide.

The difference between the saponification number of the fat before and after acetylation is the acetyl number. In case the original fat contains free soluble acids, their titer should be determined and proper correction made for the same.

Limit of error 0.50 acetyl number.

## SYNOPSIS OF REACTION

A better conception of the method may be obtained by a summary of the reactions.

Acetylation of glycerides of mono- and dihydroxy acids, mono- and diglycerides and free alcohols (see formulas).

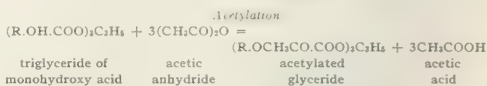
Saponification of the acetylated product (see formulas).

Saponification of the original or unacetylated product.

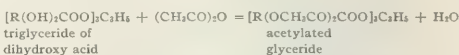
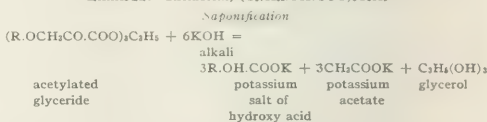
Titration of excess alkali.

Acetyl number by difference.

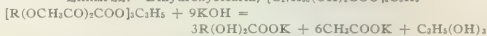
### GLYCERIDES OF MONO- AND DIHYDROXY ACIDS



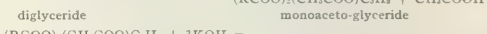
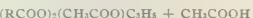
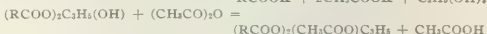
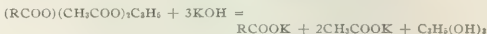
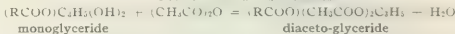
EXAMPLE: Ricinolein,  $(\text{C}_{17}\text{H}_{33}\text{O}_2\text{H.OH.COO})_2\text{C}_2\text{H}_5$



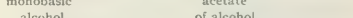
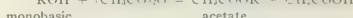
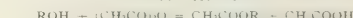
EXAMPLE: Dihydroxystearin,  $(\text{C}_{17}\text{H}_{33}(\text{OH})_2\text{COO})_2\text{C}_2\text{H}_5$



MONO- AND DIGLYCERIDES



FREE ALCOHOLS



EXAMPLES: Cholesterol phytosterol,  $\text{C}_{27}\text{H}_{48}\text{OH}$

Considerable variation is possible in writing the above formulas which, at best, poorly express the structure. In some instances the reaction is indicated at some sacrifice of form.

### CALCULATED DATA FROM THE ACETYL NUMBER

The acetyl number ( $c$ ) serves to measure the amount of hydroxy compounds in an oil, fat or wax and in case only one such compound of known molecular weight ( $m$ ) and number of hydroxyls ( $d$ ) is present, its amount ( $H$ ) can be readily calculated by the following formula:

$$H = \frac{cm}{56108d}$$

The derivation of the formula is comparatively simple. The theoretical acetyl number of a compound containing ( $d$ ) hydroxyl groups is:

$$\frac{56108d}{m}$$

The amount of such a compound in an oil, fat or wax is, therefore:

$$\frac{c}{56108d} = \frac{cm}{56108d}$$

The same results may be calculated more easily from the following table, dividing the determined acetyl number by the theoretical acetyl number or multiplying by its reciprocal:

The formation of anhydrides during the acetylating process will affect the accuracy of these calculations.

The computation of the amount of hydroxy com-

ACETYL NUMBER ON ORIGINAL PRODUCT, MASSACHUSETTS METHOD

Name	Formula	Molecular weight	Saponification number	Theoretical acetyl number	Reciprocal
<b>GLYCERIDES</b>					
Ricinolein, (C <sub>17</sub> H <sub>33</sub> OH.COO) <sub>2</sub> C <sub>2</sub> H <sub>5</sub>		932.832	180.444	180.444	0.0055419
Dihydroxystearin, (C <sub>17</sub> H <sub>33</sub> (OH) <sub>2</sub> COO) <sub>2</sub> C <sub>2</sub> H <sub>5</sub>		986.880	170.562	341.124	0.0029315
<b>MONOGLYCERIDES</b>					
Monopalmitin, (C <sub>15</sub> H <sub>31</sub> COO)C <sub>2</sub> H <sub>5</sub> (OH) <sub>2</sub>		330.304	169.868	339.736	0.0029435
Monostearin, (C <sub>17</sub> H <sub>33</sub> COO)C <sub>2</sub> H <sub>5</sub> (OH) <sub>2</sub>		358.336	156.579	313.159	0.0031933
Monolein, (C <sub>17</sub> H <sub>33</sub> COO)C <sub>2</sub> H <sub>5</sub> (OH) <sub>2</sub>		356.320	157.465	314.930	0.0031753
<b>DIGLYCERIDES</b>					
Dipalmitin, (C <sub>15</sub> H <sub>31</sub> COO) <sub>2</sub> C <sub>2</sub> H <sub>5</sub> (OH)		568.544	197.374	98.687	0.0101330
Distearin, (C <sub>17</sub> H <sub>33</sub> COO) <sub>2</sub> C <sub>2</sub> H <sub>5</sub> (OH)		624.608	179.658	89.829	0.011323
Diolein, (C <sub>17</sub> H <sub>33</sub> COO) <sub>2</sub> C <sub>2</sub> H <sub>5</sub> (OH)		620.576	180.826	90.413	0.0110604
<b>HYDROXY ACIDS</b>					
Ricinoleic, C <sub>17</sub> H <sub>33</sub> OH.COOH		298.272	188.110	188.110	0.0053160
Dihydroxystearic, C <sub>17</sub> H <sub>33</sub> (OH) <sub>2</sub> COOH		316.288	177.395	354.791	0.0028186
<b>FREE ALCOHOLS</b>					
Cholesterol, C <sub>27</sub> H <sub>46</sub> OH		386.368		145.219	0.0068862
Phytosterol, C <sub>27</sub> H <sub>46</sub> OH		386.368		145.219	0.0068862

GRAVIMETRIC PROCESS<sup>1</sup>

After acetylating, a gravimetric process for acetyl number may be conducted in a manner similar to that for the quantitative determination of insoluble fatty acids, observing all the precautions therein noted as to ceresine, washing, drying, weighing, etc.

This modification is apparently rather more difficult, tedious and subject to error than the saponification or volumetric process (Massachusetts method). A certain amount of loss arises from the dehydration of free fatty acids by acetic anhydride during acetylation, and is difficult to prevent, although of little consequence where the amount of free acids is relatively small.

The acetyl number (*a*) is calculated from the increase in weight (*i*) by the following formula:

$$a = \frac{56108i}{42.016} \text{ or } 1335.30604i$$

In case only one hydroxy compound of known molecular weight (*m*) and number of hydroxyls (*d*) is present, its amount can be calculated from the increase in weight (*i*) of the oil, fat or wax on acetylating. The theoretical increase for a hydroxy compound is:

$$\frac{42.016d}{m}$$

The amount (H) of such a compound in an oil, fat or wax is therefore:

$$H = \frac{i}{\frac{42.016d}{m}} \text{ or } \frac{im}{42.016d}$$

## MOLECULAR WEIGHT OF HYDROXY COMPOUNDS

The molecular weight of the hydroxy compounds can be calculated from the weight (*w*) of fat taken and the increase (*i*) on acetylating, provided the number (*d*) of hydroxyls in the molecule is known:

$$w : w + i = m : m + 42.016d$$

$$m = \frac{42.016dw}{i}$$

<sup>1</sup> Has not received sufficient study in this laboratory to warrant positive statements, but is similar to the methods described by Lewkowitsch (*Loc. cit.*, 1, 358-63, 466-67).

pounds by the gravimetric process is greatly facilitated by use of the following table:

ACETYL GRAVIMETRIC PROCESS ON ORIGINAL PRODUCT

Name	Molecular weight	Molecular weight after acetylating	Theoretical increase in weight per gram on acetylating <sup>(a)</sup>	Reciprocal
<b>GLYCERIDES</b>				
Ricinolein,.....	932.832	1058.880	0.135124	7.40061
Dihydroxystearin,.....	986.880	1238.976	0.255447	3.91471
<b>MONOGLYCERIDES</b>				
Monopalmitin,.....	330.304	414.336	0.254408	3.93069
Monostearin,.....	358.336	442.368	0.234506	4.26428
Monolein,.....	356.320	440.352	0.235833	4.24029
<b>DIGLYCERIDES</b>				
Dipalmitin,.....	568.544	610.560	0.073901	13.53162
Distearin,.....	624.608	666.624	0.067268	14.86591
Diolein,.....	620.576	662.592	0.067705	14.76996
<b>HYDROXY ACIDS</b>				
Ricinoleic,.....	298.272	340.288	0.140865	7.09900
Dihydroxystearic,.....	316.288	400.320	0.265682	3.76390
<b>FREE ALCOHOLS</b>				
Cholesterol,.....	386.368	428.384	0.108746	9.19574
Phytosterol,.....	386.368	428.384	0.108746	9.19574

(a) Acetyl number = 1335.30604*i*

## ACETYL NUMBER OF INSOLUBLE FATTY ACIDS

The acetyl number of the insoluble fatty acids is determined by the Massachusetts method in precisely the same way as that of the original fat. The gravimetric process is not applicable on account of the formation of anhydrides of the fatty acids. The method for preparing the stock of insoluble acids for analysis is the same as that for the determination of "Insoluble Acids," with the elimination of such features as are necessary only for quantitative work.

In order to interpret the results satisfactorily it is necessary to know the percentage of insoluble acids so that the acetyl number of the acids may be considered in conjunction with the acetyl number of the fat.

## RESULTS BY DIFFERENT METHODS

For convenience, the theoretical acetyl numbers of some hydroxy compounds by the Benedikt and Ulzer and Lewkowitsch methods are tabulated to permit comparison with the acetyl numbers by the Massachusetts and gravimetric processes previously stated. When only one hydroxy compound of known com-

## ACETYL NUMBER ON ACETYLATED PRODUCT, BENEDIKT AND ULZER AND LEWKOWITSCH METHODS

Name (Acetylated)	Formula	Molecular weight	Saponification number	Theoretical acetyl number	Reciprocal
<b>GLYCERIDES</b>					
Ricinolein, $(C_{17}H_{31}O_2CH_2CO_2COO)_3C_3H_5$		1058.880	317.928	158.964	0.0062907
Dihydroxystearin, $[C_{17}H_{31}(OCH_2CO_2COO)_2]_2C_2H_5$		1238.976	407.572	271.715	0.0036803
<b>MONOGLYCERIDES</b>					
Monopalmitin, $(C_{15}H_{31}COO)(CH_2COO)_2C_3H_5$		414.336	406.250	270.833	0.0036923
Monostearin, $(C_{17}H_{33}COO)(CH_2COO)_2C_3H_5$		442.368	380.507	253.671	0.0039421
Monolein, $(C_{17}H_{33}COO)(CH_2COO)_2C_3H_5$		440.352	382.249	254.832	0.0039242
<b>DIGLYCERIDES</b>					
Dipalmitin, $(C_{15}H_{31}COO)_2(CH_2COO)C_3H_5$		610.560	275.688	91.896	0.0108819
Distearin, $(C_{17}H_{33}COO)_2(CH_2COO)C_3H_5$		666.624	252.502	84.167	0.0118811
Diolein, $(C_{17}H_{33}COO)_2(CH_2COO)C_3H_5$		662.592	254.039	84.680	0.0118092
<b>HYDROXY ACIDS</b>					
Ricinoleic, $C_{17}H_{31}O_2CH_2CO_2COOH$		340.288	329.768	164.884	0.0060649
Dihydroxystearic, $C_{17}H_{31}(OCH_2CO_2COO)_2COOH$		400.320	420.474	280.316	0.0035674
<b>FREE ALCOHOLS</b>					
Cholesterol, $C_{27}H_{47}O_2CO_2C_3H_5$		428.384		130.976	0.0076350
Phytosterol, $C_{27}H_{47}O_2CO_2C_3H_5$		428.384		130.976	0.0076350

position is present in an oil or fat, the results can be readily converted from the basis of the original to that of the acetylated product and *vice versa*. In other cases conversion is generally impracticable on account of the marked differences in assimilation of acetyl by the several classes of hydroxy compounds. Formulas may show the relation, however, that the results by different methods bear to each other, (*m*) indicating the molecular weight of the hydroxy compound, (*d*) the number of hydroxyls, and (*i*) the increase in weight on acetylating:

## Massachusetts Method Gravimetric Method

cm	im
56108d	42.016d

## Benedikt and Ulzer and Lewkowitsch Methods

$$(m + 42.016d)$$

$$56108d$$

## SUMMARY

The acetyl numbers of a fat and of the insoluble acids afford valuable information relative to the nature and the quality of a product. Apparently many analysts have been deterred from making the determinations on account of the time required, tedious manipulation involved or inability to interpret the results. The proposed method is comparatively short and simple and readily understood because of its similarity to other fat methods in common use. It is practically free from the objections cited for the earlier methods and the results are directly comparable with other fat determinations, being on the same basis.

MASSACHUSETTS AGRICULTURAL EXPERIMENT STATION  
AMHERST

A COMPARISON OF NEUTRAL AMMONIUM CITRATE WITH SODIUM CITRATE AND *N*/10 CITRATE ACID<sup>1</sup>

By PAUL RUDNICK, W. B. DERBY AND W. L. LATSHAW

Since the appearance of a previous paper<sup>2</sup> on the subject of neutral ammonium citrate, the use of sodium citrate as a substitute for ammonium citrate has been proposed by Bosworth.<sup>3</sup> The values obtained by him with a solution of sodium citrate of the same molar concentration as the official ammonium citrate solution are, however, not in good concordance with those

obtained by neutral ammonium citrate. This fact was further confirmed by us in the determinations on a sample of acid phosphate shown in Table I.

These determinations were made substantially according to the official methods of the A. O. A. C.,<sup>1</sup> except that the neutral ammonium citrate solution was prepared as described in our previous paper.<sup>2</sup> The phosphoric acid was in all cases determined by the volumetric molybdate method. The proportions of reagent, whether neutral ammonium citrate, sodium citrate or *N*/10 citric acid, to the weight of sample taken, were the same as in the official method.

TABLE I.—DETERMINATION OF INSOLUBLE PHOSPHORIC ACID WITH SODIUM CITRATE AND NEUTRAL AMMONIUM CITRATE

Sodium citrate.....	1.46%	Ammonium citrate.....	0.30%
AV.....	1.42		0.34
	1.44		0.32

The specific gravity of this sodium citrate solution was 1.163 as against 1.09 for neutral ammonium citrate solution. Various trials showed that more concentrated solutions of sodium citrate give results approaching more nearly those obtained by the use of neutral ammonium citrate, as shown in Table II.

TABLE II.—DETERMINATION OF INSOLUBLE PHOSPHORIC ACID IN ACID PHOSPHATE WITH VARYING CONCENTRATIONS OF SODIUM CITRATE AS COMPARED WITH AMMONIUM CITRATE

Ammonium citrate.	G. per l.	Specific gravity	Percentages			
			1	2	3	4
		1.09	0.53	2.58	0.77	0.62
				2.62	..	0.65
Sodium citrate.....	80.0	1.043	1.83			
	159.5	1.084	..	3.14	..	..
	178.5	1.093	..	..	..	1.53
						1.59
	247.7	1.123	..	3.06	..	..
	293.8	1.147	..	..	..	1.28
						1.37
	312.8	1.153	..	2.99	..	..
	326.6	1.163	..	..	..	..
	444.0	1.220	..	2.92	..	..
	496.8	1.231	0.92	..	..	..
	568.8	1.282	..	..	0.49	..
					0.46	..

NOTE.—The concentration of sodium citrate is expressed in grams of crystallized sodium citrate  $[(C_6H_5O_7Na)_3 \cdot 11H_2O]$  per liter.

The disadvantages of working with such heavy solutions suggested the possibility of using a citric acid solution of suitable concentration as a substitute. After trying various strengths ranging from two per cent, as used for basic slag analyses, downward, it was found that a *N*/10 solution of citric acid gave results approximating quite closely to those obtained with neutral ammonium citrate. The results are shown in Table III.

<sup>1</sup> Presented at the 49th Meeting of the American Chemical Society, Cincinnati, April 6-10, 1914.

<sup>2</sup> This JOURNAL, 5 (1913), 1013.

<sup>3</sup> Ibid., 6 (1914), 227.

<sup>1</sup> Rev. Bur. of Chem., Bull. 107, pp. 1-5.

<sup>2</sup> This JOURNAL, 5 (1913), 1013.



TABLE III—DETERMINATION OF INSOLUBLE PHOSPHORIC ACID WITH N/10 CITRIC ACID AND NEUTRAL AMMONIUM CITRATE (PERCENTAGES)

	Neutral ammonium citrate	N/10 citric acid		Neutral ammonium citrate	N/10 citric acid
Acid phosphate	1.60	1.50	Raw bone meal	18.75	20.50
Av.	1.88	1.43		18.75	20.35
	1.50	2.48	Av.	18.75	20.42
Acid phosphate	2.07	1.94	Complete fertilizer	1.64	1.57
	2.01	1.95		1.60	1.55
Av.	2.04	1.95	Av.	1.62	1.56
Tankage	6.53	6.90	Complete fertilizer	0.14	0.23
	6.49	6.88		0.18	0.25
Av.	6.51	6.89	Av.	0.16	0.24

N/10 citric acid, therefore, is entitled to careful consideration as a promising substitute for neutral ammonium citrate solution, as it not only gives results substantially identical with those obtained with the present official reagent for determining insoluble phosphoric acid, but has, moreover, at least two important advantages over ammonium citrate:

1—N/10 citric acid is much more easily prepared and standardized than neutral ammonium citrate solution.

2—Extraction with N/10 citric acid is as easy and rapid as with hot water, the time of filtration, particularly in bone, tankage and complete fertilizers, being cut down to a very few minutes.

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## THE EFFECT OF ENSILAGE FERMENTATION AND ANIMAL DIGESTION ON THE SOLUBILITY OF PHOSPHORIC ACID IN PHOSPHATE ROCK

By C. A. MOORE

Received March 20, 1914

A recent article<sup>1</sup> by Forbes and Fritz reports some laboratory results which indicate that the ensilage process may be used to render floats soluble and hence available both to animals and plants. With the object of showing the practical extent to which the solubility of the rock was increased, the writer has prepared Table I from their data. The table should be considered, however, as at best only a close approximation, for the article referred to did not furnish either the composition of the phosphate rock or other data which would have been of value in this connection. In making the calculations of Table I, the writer assumed the floats to contain 14 per cent of P, and that there were used 83 parts, by weight, of green silage corn to 1 part of floats. According to this table, 0.2

TABLE I—CALCULATIONS BASED ON FORBES AND FRITZ TABLE

Material	Amount of dry matter taken for basis of calculation Grams	Inorganic P soluble in 0.2 per cent HCl		Inorganic P soluble in 0.2 per cent HCl per gram of phosphate rock Gram
		Total P Gram	P Gram	
Green corn (whole plant)	83.0	0.1718	0.0689	
Green corn	83.0	0.3118	0.1445	0.0756
Phosphate rock	1.0			
Ensilage	76.7	0.1718	0.0851	....
Ensilage	81.2			0.1073
Phosphate rock	1.0	0.3118	0.1924	

per cent HCl dissolved 54.0 per cent of the P of the floats when mixed with the green silage corn, but before passing through the ensilage process, and 76.65 per cent after going through the ensilage process. This amounts, therefore, to an increased solubility of 3.17 pounds of P, or 7.26 pounds of  $P_2O_5$  per 100 pounds of phosphate rock (floats).

<sup>1</sup> THIS JOURNAL, 6 (1914), 222, 223.

In the proportions used by Forbes and Fritz, a 100-ton silo would require 800 pounds of floats, a quantity which, even with full allowance for the increased solubility, would amount to a moderate application for only two acres. Not to mention the very narrow margin of profit which this indicates, two questions arise at this point: (1) Would there be any detrimental effect on the feeding value of ensilage treated with floats? (2) What would be the effect of the process of animal digestion on the solubility of the floats?

To answer the first question satisfactorily would require many more data than the author has at hand, but Table II gives the results of some feeding experiments made at the Tennessee Agricultural Experiment Station in 1909. In these experiments about 2 pounds of finely ground phosphate rock were mixed with

TABLE II—FEEDING TEST OF ENSILAGE TREATED WITH FLOATS AS COMPARED WITH UNTREATED ENSILAGE

The "treated" ensilage was prepared by mixing about 2 lbs. of finely ground phosphate rock with 100 lbs. of chopped corn (whole plant) at time silo was filled.

silo was filled		Weight of animal Lbs.	Feed per day		
Date (1909)	Animal		Ensilage Lbs.	Cottonseed meal Lbs.	Ensilage unclean Lbs.
Ensilage containing floats					
Feb. 2	Cow No. 30	875	38	2	5
Feb. 3	Cow No. 30		28	2	18
Feb. 4	Cow No. 30		22 1/2	2	16
Feb. 5	Cow No. 30		20	2	14
Feb. 6	Cow No. 30	810	10(a)	2	10
Feb. 2	Blue heifer	480	22 1/2	1	21 1/2
Feb. 3	Blue heifer		22 1/2	1	4
Feb. 4	Blue heifer		20	1	1
Feb. 5	Blue heifer		20	1	7
Feb. 6	Blue heifer	403	10(a)	1	4 1/2
Ensilage without floats					
Feb. 2	Cow No. 10	1000	44 1/2	2	0
Feb. 3	Cow No. 10		45	2	0
Feb. 4	Cow No. 10		45	2	0
Feb. 5	Cow No. 10		45	2	0
Feb. 6	Cow No. 10	990	22 1/2(a)	2	0
Feb. 2	Fawn heifer	460	25	1	0
Feb. 3	Fawn heifer		28	1	0
Feb. 4	Fawn heifer		28	1	0
Feb. 5	Fawn heifer		28	1	1
Feb. 6	Fawn heifer	480	12 1/2(a)	1	2 1/2

(a) Morning feed only.

NOTE—Both groups were fed plain ensilage and meal for two days previous to beginning of record, each animal eating the amounts given for Feb. 2 without waste for that period.

every 100 pounds of the corn at the time that the silo was filled. The results show plainly that in this case too much rock was present, for the animals soon refused to eat more than a small part of the treated ensilage, although its odor and appearance indicated excellent material.

In connection with the feeding experiment, some data were obtained bearing on the second question, in regard to the availability of the  $P_2O_5$  of the phosphate rock when voided by the animals. Samples of dung were saved from each animal, and Table III gives the per cent of total  $P_2O_5$  in each sample when calculated to a moisture-free basis. Assuming that

TABLE III—TOTAL PHOSPHORIC ACID ( $P_2O_5$ ) IN DUNG FROM ANIMALS USED IN FEEDING EXPERIMENT

Animal	Kind of feed	Results on moisture-free basis	
		P <sub>2</sub> O <sub>5</sub>	Per cent in dung
Cow No. 10	Cottonseed meal and unphosphated ensilage	1.17	
Cow No. 30	Cottonseed meal and phosphated ensilage	5.95	
Fawn heifer	Cottonseed meal and unphosphated ensilage	1.78	
Blue heifer	Cottonseed meal and phosphated ensilage	9.34	

with the same kind of feed the dung from the cows would be of similar composition, and that in like manner the dung from the heifers would be com-

parable, the amounts of phosphate rock in the dung of cow No. 30 and of the blue heifer were calculated from the analyses given in Table III. Table IV gives the quantities of the various materials taken, the amount of 0.1 per cent citric acid used as a solvent, and the percentages of  $P_2O_5$  found. The finely ground phosphate used throughout contained 32.0 per cent of  $P_2O_5$ . The citric acid solution was shaken up in contact with the material for two days and filtered, and the  $P_2O_5$  in the filtrate determined. From these determinations the calculation was made that the combined action of the ensilage process and the process of animal digestion resulted in an increase of 0.93 pound of  $P_2O_5$  per 100 pounds of the rock in the case of the cow and 1.17 pounds in the case of the

TABLE IV—PHOSPHORIC ACID ( $P_2O_5$ ) SOLUBLE IN 1000 CC. OF 0.1 PER

CENT CITRIC ACID  
All percentages are calculated on a uniform basis of moisture-free and phosphate-free manure, *i. e.*, the plain manure from the unphosphated feed (15.0 grams) is taken as the basis of comparison.

Material	Quantity used for analysis (Water-free basis) Grams	$P_2O_5$ found Per cent
Dung from cow No. 10 (unphosphated ensilage)	15.0	0.76
Dung from cow No. 10.....	15.0	0.88
Phosphate rock.....	2.7137	1.05
Dung from cow No. 30 (phosphated ensilage).....	17.7137	1.38
Dung from fawn heifer (unphosphated ensilage)	15.0	1.47
Dung from fawn heifer.....	15.0	1.86
Phosphate rock.....	4.9256	
Dung from blue heifer (phosphated ensilage).....	19.9256	

Notes.—A water solution of manure is normally alkaline and hence much of the "available"  $P_2O_5$  is in a precipitated form. Only a slightly acid solution is necessary in order to get a marked increase in soluble  $P_2O_5$ . 2—If manure be treated with a 0.1 per cent citric acid solution in the proportions used, the solution is apt to become alkaline in the course of a few days, due to the production of  $NH_3$  by bacteria; hence long standing must be avoided.

heifer. The increase in soluble  $P_2O_5$  was, therefore, very small. On the assumption that all of the phosphoric acid was voided in the dung, these results, taken into consideration with those of Forbes and Fritz, indicate a reversion of the  $P_2O_5$  made soluble by the ensilage.

#### SUMMARY

1—From calculations based on work reported by Forbes and Fritz, 22.65 per cent of the total phosphoric acid of phosphate rock (floats) was rendered soluble in 0.2 per cent HCl through the ensilage process, 1 part of rock being used to 250 parts of green silage corn.

2—Feeding experiments by the author proved that when 2 pounds of finely ground phosphate rock were mixed with 100 pounds of green silage corn at time of filling of the silo, the resultant ensilage, though excellent in odor and appearance, was not suitable to be fed in ordinary amounts, the animals soon refusing to eat it.

3—The solubility in 0.1 per cent citric acid of the  $P_2O_5$  of the phosphate rock in the dung of the animals fed phosphated ensilage was increased only 3.28 per cent of the total  $P_2O_5$  as an average of two trials.

4—Based on the assumption that all of the phosphoric acid was voided in the dung, the data at hand indicate that a reversion of the soluble  $P_2O_5$  took place during the process of animal digestion.

5—The general conclusion is indicated that the silo does not offer a practical means of making the  $P_2O_5$  of phosphate rock available for plant use.

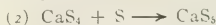
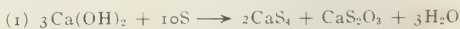
## THE THEORETICAL BASIS FOR THE PROPORTIONS OF LIME AND SULFUR USED IN THE COMMERCIAL PREPARATION OF THE LIME-SULFUR SPRAY

By HERMAN V. TARTAR

Received March 11, 1914

Various formulas (*i. e.*, proportions of lime, sulfur and water) have been recommended for use in the preparation of the commercial lime-sulfur spray. In the early literature on this subject, the proportions of lime (CaO) and sulfur vary within wide limits; the more recent work<sup>1</sup> shows the proper ratio of lime to sulfur to be approximately 1:2. There are, however, some differences still existing among the recommendations made in this connection by the different agricultural experiment stations. It is well known, too, that various factors such as concentration and length of time of boiling, have an influence on the amounts of lime and sulfur required. Even the length of time of cooling, following the boiling period, modifies the composition of the solution and consequently the requirements of raw material. For example, in one of the experiments at our local station plant where 108 gallons of material were prepared, a sample taken and immediately cooled just at the close of the cooking period had a gravity of 33°, while one taken after the solution had cooled in the tank for 12 hours, had only a 30° strength. This decrease in gravity was due, no doubt, to the decomposition of calcium thiosulfate in the hot solution. Similar experiments, in which the entire solution was cooled immediately after boiling, showed no decrease in gravity upon standing. Because of these numerous factors which influence the composition of the spray, the formulas given by different investigators have been worked out largely by the "cut and try" method. Different amounts of lime, sulfur and water have been cooked for various lengths of time and from the analyses made of the resulting solutions and sediment (sulfite), the formulas have been derived. But little, if any, attention has been given to the exact chemical reactions which occur.

To all familiar with this subject, it is very evident that any formula used in making lime-sulfur must necessarily be based on the reactions taking place. Investigations carried out in this laboratory<sup>2</sup> have shown that these reactions are represented by the following equations:



There is also some oxidation of the polysulfides when the material is exposed to the air but this is so slight, under ordinary conditions of commercial preparation, where large, tall cooking vats are used, that it need not be considered here. The knowledge of the exact nature of these chemical reactions affords a theoretical basis for determining the proportions of lime and sulfur required in the preparation of a given sample of lime-

<sup>1</sup> Cordley, unpublished results of this station; Stewart, Penn. Agr. Exp. Sta., Bull. 99; Van Slyke, N. Y. Agr. Exp. Sta. (Geneva), Bull. 339.

<sup>2</sup> Jour. Amer. Chem. Soc., 27 (1914), 495.

sulfur. This will be brought out in the discussion which follows.

It will be seen from the equations given above that the compounds formed by the reaction between calcium hydroxide and sulfur, under ordinary commercial conditions of manufacture, are calcium tetrasulfide, pentasulfide, thiosulfate, and sulfite. All of these compounds are readily soluble in water with the exception of the sulfite, which is comparatively insoluble. This being true, the chemical analysis of the lime-sulfur solution shows the amounts of lime (slaked with water to form hydroxide) and sulfur that have reacted in the formation of the same except the amounts of these substances necessary to form the insoluble sulfite produced. From the knowledge of the chemical reactions that occur, however, it is not a difficult matter to estimate, from the chemical analysis of the solution, the quantity of sulfite which has been formed. Equation (1) shows that when calcium hydroxide and sulfur combine, one-third of the calcium is combined as thiosulfate and two-thirds as polysulfide. Since there is no decomposition of the polysulfide, the quantitative estimation of the calcium combined in this form gives a means for determining the amount of thiosulfate which has been formed. The difference between this total estimated amount of thiosulfate and the amount actually present in the solution, is the quantity that has decomposed; and from this data the amount of sulfite can be easily calculated. The initial ratio of lime to sulfur is also easily determined when one knows not only the amounts of calcium and sulfur present in a given lime-sulfur solution, but also the insoluble sulfite produced in the preparation of the same.

The analytical methods for determining the amounts of calcium combined as polysulfide as well as the amounts of other constituents of lime-sulfur, have been very thoroughly worked out<sup>1</sup> and it is unnecessary to discuss them in this paper.

The actual application of the discussion given above is brought out in Table I. The chemical compositions of several samples of commercial lime-sulfur solution are given; also the estimated amounts of insoluble calcium sulfite formed and the calculated ratios of lime

dilute solutions prepared under commercial conditions. It is evident, however, from the work of Thatcher<sup>1</sup> and Van Slyke<sup>2</sup> that the ratio in this case would be somewhat greater than 1 : 2; in some cases it would be perhaps 1 : 2.25.

The theoretical basis given here will not exactly apply, of course, to the preparation of small amounts of solution, say 150 gallons or less, where the oxidation of the polysulfides occurs to a considerable extent through contact with the air.

Acknowledgment is due to Mr. R. H. Robinson who made several of the chemical analyses reported above.

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## THE DETERMINATION OF CAMPHOR IN TABLETS AND PILLS

By EDWIN DOWZARD

Received March 9, 1914

In so far as the writer has been able to learn, the methods used elsewhere for the determination of camphor in tablets and pills have not proved satisfactory. For this reason a description of a method is given which has been in use for over five years with satisfactory results:

Camphor may be rapidly and completely removed from tablets and pills by distillation in a current of steam. The watery distillate contains both dissolved and undissolved camphor, which can be extracted with benzol. By determining the optical rotation of the benzol solution, the amount of camphor present in the tablets or pills can be readily calculated.

A special apparatus is required for the distillation, because an ordinary condenser cannot be used as the camphor blocks up the tube.

After a number of trials the arrangement shown in the figure proved satisfactory.

The apparatus consists of a flask, *A*, for generating steam, a second flask, *B*, for the steam distillation, and a receiver, *C* (a retort with the tube bent as shown), for the distillate.

The retort is kept cool by two streams of water (*D* and *E*). *D* impinges on the wide part of the neck, and *E* on the extreme end of the tube, which is closed with a rubber stopper fitted with a glass tube open at both ends; thus every part of the retort is kept covered with a film of water, ensuring a complete condensation. The large funnel *F* conveys the water to a sink by means of a rubber tube.

The funnel should be kept about half filled with water, the flow of water from the funnel being regulated by pinchcock *G*.

**PROCEDURE FOR A DETERMINATION**—A number of tablets or pills containing about 2½ to 3 grams of camphor are placed in the flask *B*. The tablets are just covered with water and the apparatus connected. Sufficient water to cover the bottom of the tube *H* is placed in the retort.

The water in *A* is now boiled, with *I* closed, the steam passing into *B* through the tube, which almost

TABLE I—CHEMICAL COMPOSITION OF LIME-SULFUR SOLUTION  
LIME (CaO) SULFUR (S)

No.	Sr.	Gr.	Combined as			Combined as			RATIO CaO : S
			Poly- sulfide	Thio- sulfate	Estimated as insol.	Poly- sulfide	Thio- sulfate	Estimated as insol.	
1.	1.	2.585	9.464	1.820	4.060	26.313	2.080	2.320	1 2.00
2.	1.	3.335	13.943	0.672	5.152	37.498	0.768	2.944	1 2.08
3.	1.	2.825	11.357	1.120	4.558	30.780	1.280	2.604	1 2.03
4.	1.	2.560	10.248	1.008	4.116	27.926	1.152	2.354	1 2.04
5.	1.	2.820	11.424	0.840	4.872	31.283	0.960	2.784	1 2.04
6.	1.	3.110	11.802	1.198	4.703	31.930	1.370	2.688	1 2.04
7.	(a)	10.	8.334	1.286	4.131	28.980	1.470	2.360	1 2.01

(a) Not determined

to sulfur. The results relating to chemical composition are expressed as grams per 100 cc. of solution.

The data given show that the proportion of lime (CaO) to sulfur which react in the preparation of the more concentrated commercial lime sulfur solutions is but a mere trifle greater than 1 : 2. Unfortunately the author has not had opportunity to examine more

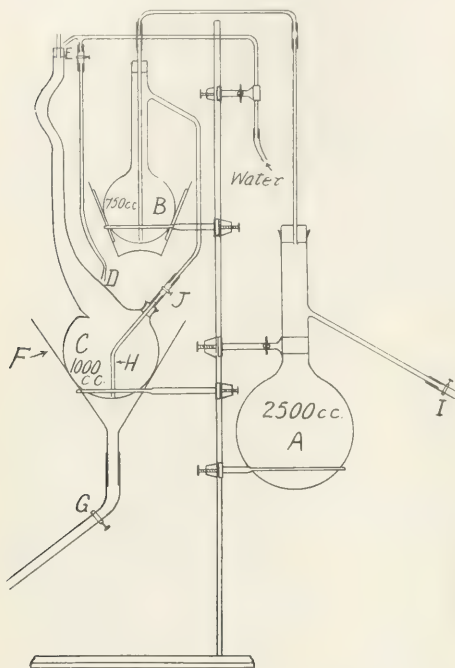
<sup>1</sup> Jour. Amer. Chem. Soc., 27 (1905), 244; THIS JOURNAL, 2 (1910), 271; Mich. Agr. Exp. Sta., Tech. Bull. No. 6.

<sup>1</sup> Jour. Amer. Chem. Soc., 30 (1908), 63.

<sup>2</sup> Loc. cit.



touches the bottom of the flask, carries over the camphor from the disintegrated tablets. The distillation is continued until the distillate measures about 500 cc.



The pinchcock *I* is now opened and the flame removed from *A*. The water is allowed to run over the retort for 5 minutes longer to thoroughly cool the distillate.

The retort is now disconnected, leaving the tube *H* with the pinchcock *J* attached and screwed tight; 25 cc. of benzol measured at 25° C. are allowed to flow into the retort through the neck, after removing the rubber stopper fitted with the glass tube opened at both ends. The retort is securely closed with a rubber stopper and the contents vigorously agitated for several minutes. The position of the retort should be frequently changed to allow the benzol to reach every part, thus ensuring that all the camphor is dissolved in the benzol. The mixture is transferred to a separator, the water drawn off, and the benzol solution of camphor filtered through a small plug of cotton wool into a 100 mm. tube, the rotation being taken at 25° C.

If the pills or tablets do not disintegrate readily, they should be coarsely ground in a mortar, before distilling.

The writer has determined the rotation of a number of samples of camphor. All examined had practically the same rotation.

The following figures give the camphor equivalent in 50 cc. of benzol solution for each 0° 1' of rotation:

Rotation taken in 100 mm. tube at 25° C.			
Grams camphor dissolved in benzol	Total volume cc.	Rotation	Camphor
6	50	0° 1'	= 0.019402
3	50	0° 1'	= 0.019745
1.5	50	0° 1'	= 0.019692

Average 0° 1' = 0.019613 gram of camphor in 50 cc. or 0.009806 gram camphor in 25 cc. for each 0° 1' of rotation.

To test the apparatus, 2 grams of camphor were distilled and the distillate extracted with 25 cc. of benzol, as described. The following figures were obtained:

Rotation in 100 mm. tube at 25° C. = 3° 5' or 185°

As the above solution consists of 2 grams of camphor and 25 cc. of benzol, not 25 grams made up to 25 cc., a correction is necessary and is determined as follows:

$$185' \times 0.009806 = 1.8144$$

From the figures previously obtained, we know that the above rotation indicates the presence of 1.8144 grams of camphor in 25 cc. of the solution. It is now necessary to calculate how much benzol we have in 25 cc. of this solution.

As the specific gravity of camphor at 25° C. is about 0.99, 1.8144 grams of camphor displace 1.8324 cc.

$$\frac{1.8144}{0.99} = 1.8324$$

Therefore, we have 23.1676 cc. of benzol in 25 cc. of the solution

$$\frac{25.0000 \text{ cc.}}{1.8324 \text{ cc.}}$$

$$23.1676 \text{ cc.}$$

Now if 23.1676 cc. of benzol have 1.8144 grams of camphor, 25 cc. will have 1.957 grams.

$$\frac{1.8144 \times 25}{23.1676} = 1.957$$

or, 97.85 per cent of the amount taken.'

Several determinations were made with varying amounts of camphor, with very close results. It will be seen that a slight correction is necessary for loss.

As each apparatus and the manipulation of different chemists will vary somewhat, several determinations, using known weights of camphor, should be made and the factor for the apparatus calculated.

The factor for the apparatus used by the writer is 0.01001 gram of camphor for each 0° 1' of rotation in 100 mm. tube at 25° C.

The average amount of camphor in the tablet or pills is obtained by dividing the number taken into the weight of camphor found.

Using the above method, a determination may be completed within two hours.

ANALYTICAL DEPARTMENT, PARKE, DAVIS & CO.  
DETROIT, MICHIGAN

## LABORATORY AND PLANT

### THE STATUS AND TENDENCY OF THE GAS INDUSTRY<sup>1</sup>

By WALTER R. ADDICKS

The artificial gas business was never in so advantage-

<sup>1</sup> Presented at the meeting of the N. Y. Section of the Society of Chemical Industry, The Chemists Club, March 27, 1914.

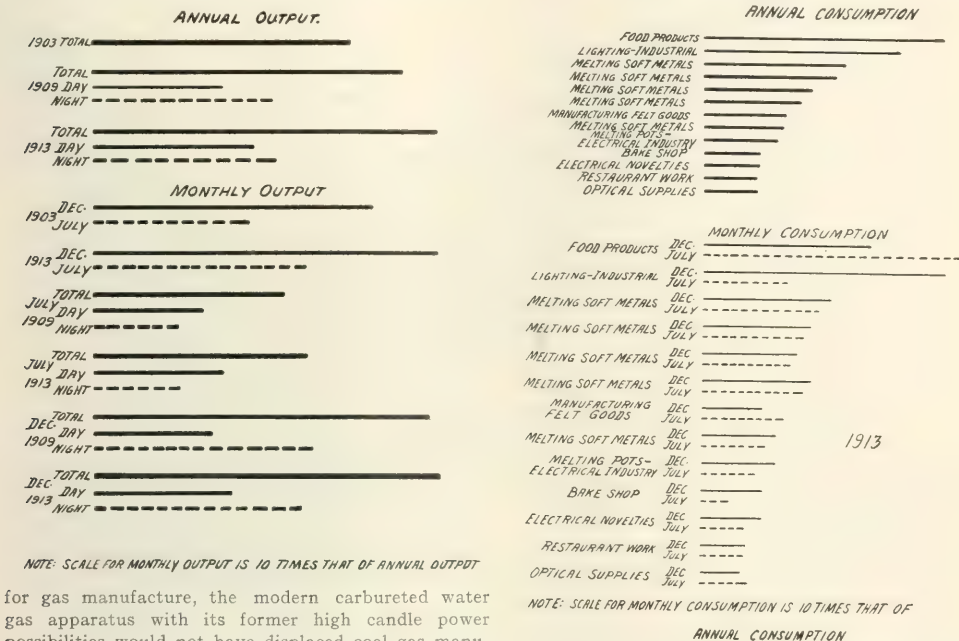
ous a position strategically as at this writing, yet two influences are felt adverse to progress: the first is an obsolete candle power standard; the second, which is not confined to the gas industry, a tendency to deny to proprietorship a percentage return on investments commensurate with the character of the service and

the ability of management necessary to produce results demanded by modern conditions.

Had the incandescent gas mantle, equally useful for coal or carburetted water gas, been invented and perfected before the advent of a supply of cheap oil

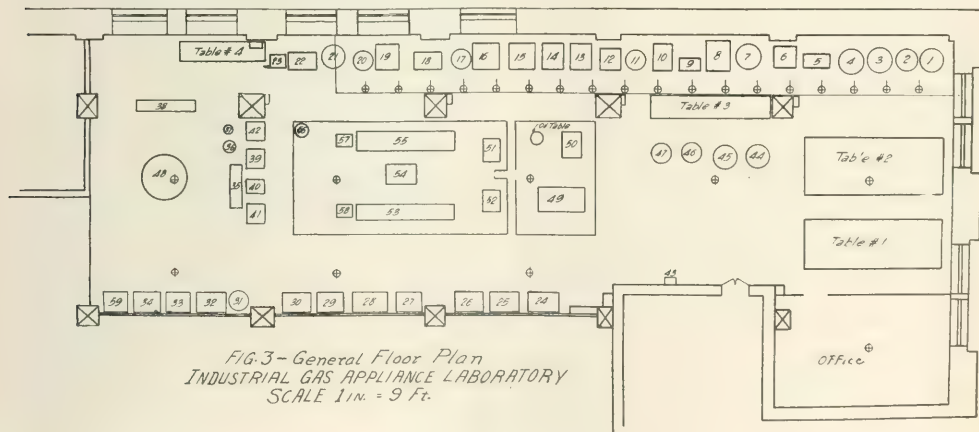
affected the supply of oil for carbureted water gas manufacture, coal gas, while still an ultimate, would not as yet be an immediate necessity to the gas busi-

DIAGRAM SHOWING APPROXIMATE TYPICAL LARGE CONSUMERS OF GAS.



for gas manufacture, the modern carbureted water gas apparatus with its former high candle power possibilities would not have displaced coal gas manufacture or have reached its present important place in the gas industry; it is also probable that electricity would not have had its encouragement to enter the

ness. These observations are made to direct your attention to a study of cause and effect in the gas industry.



lighting field, the first important step in electrical development. Had the perfection of operation of the automobile followed by other natural mechanical developments involving large consumption of oil not

Electricity has forged ahead in the lighting field and the power field, but in the heating field gas holds a stronger position than ever before, and it is still no mean competitor of electricity in the lighting and

No. U. S. PAT. No.	TRADE No.	KIND OR APPLIANCE	Max. gas consump- tion per hr.	Practical range of working temperature	
			Cu. ft.	F.	
SOME USEFUL, NOT ALL					
BURNERS					
Table No. 3	103	High power burner	175		Melting gum, heating cylinders, tinning, soldering, floor finish, replacing coal in confectionery stores, raising steam, candy manufacture, annealing, smoking meats,
	68	Cyclone burner	75		heating rubber compounds, etc., hat drying, heating plating tanks, drying photos, umbrella steaming, syrup manufacture, heating plating and singeing ovens, steam boilers, cold cream, etc.; bending glass, etc.; drying nuts, foodstuffs, etc.; soap manufacture, glue manufacture, melting metals, heating water-jacketed kettles, manu-
	157	Mounted burner	150		facturing ink, heating drying tanks, heating oil, drying blue-prints, hot water for soda fountains, singeing, hat renovating, feather steaming, pitch kettles, general boiling, sterilizing, heating, sweating on tables, sawdust drying, embossing, wood drying, brush drying, drying vats, kegs, etc.; china and glass kilns, japanning, lac-
	733 B	Hot plate burner	60	BURNERS 150 to 1800	quering and general drying ovens; drying feathers, bending wood, paint burning, testing oil, general roasting
	732 B	Hot plate burner	40		
	731 B	Hot plate burner	20		
	105	High power burners	300		
	34	Solid type burner	700		
	13	Triple industrial burner	300		
	106	High power burner	200		
Table No. 4	113	Pipe burner 1 1/2" X 30"	100		
	119	Pipe burner 2" X 36"	200		
	000	Hand blow torch	25		
	00	Hand blow torch	35		
	0	Hand blow torch	40	200 to 2000	
	1	Hand blow torch	50		
	2	Hand blow torch	100		
	3	Hand blow torch	150		
	81	Hand blow torch	30		
	82	Hand blow torch	75		
Table No. 1	83	Hand blow torch	100		
	84	Hand blow torch	175		
	85	Hand blow torch	235		
	8 B	Hand blow torch	15		
	8 C	Hand blow torch	30		
	8 E	Hand blow torch	50		
	8 F	Hand blow torch	100		
	109	Pipe burner 1 1/4" X 24"	30		
	105	Pipe burner 1" X 18"	30		
	101	Pipe burner 3/4" X 12"	15		
Table No. 2	148	Pipe burner 1" X 18"	15	BURNERS 150 to 1800	
	91	Longitudinal burner	75		
	146	Mounted burner	75		
	140	Mounted burner	20		
	147	Mounted burner	35		
	142	Mounted burner	18		
	149	Mounted burner	60		
		3-ring concentric burner	100		
		3/4" core with 8 No. 7 Bunsens	100		
	2	Adjustable burner	15		
Table No. 1	8	Adjustable burner	25		
	4	Students' burner	10		
	6	Bunsen burner	10		
	5	Standard burner	15		
	3	Handy burner	8		
	61	Cyclone burner	15		
	62	Cyclone burner	20		
	51	Bunsen burner	5		
	52	Bunsen burner	7		
	53	Bunsen burner	8		
Table No. 2	000	Stand blow torch	5		
	00	Stand blow torch	15	200 to 2000	
	0	Stand blow torch	40		
	1	Stand blow torch	50		
	2	Stand blow torch	100		
	3	Stand blow torch	150		
	1	Buzzer soldering iron heater	15	200 to 1500	
	2	Buzzer soldering iron heater	50		
	101	Johnson soldering iron heater	30		
	410 A	Soft metal furnace	40	250 to 800	
Table No. 2	626	Glue heater	15		
	17	Candy batch warmer	35	120 to 150	
		2 ft. ribbon burner	200	200 to 1000	
	6	Soft metal burner	250	200 to 1600	
	93	Longitudinal burner	150	200 to 1600	
	10	Cluster burner	200	200 to 1000	
	4	Umbrella burner	50	200 to 1000	
	3	Pattern radiator burner	100	200 to 1000	
	2	Babbitt melter	60	400 to 1700	
		Two motor heads	150 ea	200 to 2000	
Table No. 2		Soldering iron heater	25	200 to 1500	
		Soldering iron heater	40	200 to 1500	
		Bench forge	25	1000 to 2300	
	2	Bench forge	100	1000 to 2300	
	1	Bench forge	25	1000 to 2300	
		3-quart glue heater	10	150	
	3	Soldering iron heater	60	200 to 1500	
	1	Muffle furnace	50	1000 to 2300	
	17	Rivet heater	100	1000 to 2300	
	1	Soft metal furnace	90	1000 to 1700	
Table No. 2		Melting furnace	25	1000 to 2200	
	1	3 1/2 H. P. steam boiler with standard automatic water feeder and feed water heater	280		
	2	1 H. P. steam boiler, with Lawler water feeder	100		
	3	Steam superheater	75		
	4	40 gal. copper-jacketed kettle—tinned	150		
	5	Sanitary vacuum cleaner	150		
	6	22 3 H. P. steam boiler, with Lawler water feeder	240		
	7	Melter	100	1000 to 2500	
	8	Round annealer	100	1000 to 1600	
	9	Bar annealer	75	1000 to 1600	
Table No. 2	10	Forge	125	1000 to 2500	
	11	Tool room forge	100	1000 to 2500	
	12	Oil tempering furnace with hood	50	200 to 1000	
	13	Oven furnace	250	1000 to 2000	
	14	Tempering furnace	200	1000 to 1500	
	15	Rivet heater	200	1500 to 2800	
	16	Muffle furnace	200	1000 to 1500	
	17	Oven furnace	240	1000 to 2400	
	18	Lead hardening	95	1000 to 1800	
	19	Soft metal furnace	125	1000 to 1600	
Table No. 2	20	Muffle furnace	125	1000 to 1600	
	21	Portable melter	20	600	
	22	Soft metal furnace	150	200 to 800	
	430 A	Soft metal furnace	150	200 to 800	
Blow TORCHES					
General brazing, soldering, bending, hardening, annealing, shaping.					
STEAM BOILERS					
Garment manufacture, casket manufacture, necktie manufacture, vulcanizing, cleaning jewelry, draperies, feather, glove and hat manufacture; plating, glue, umbrella lace drying rooms, silks and velvets, jacketed kettles, button manufacture; extracts and fruit, syrups, etc. Bakers, restaurants, sterilizing, distilling, butter melting, paper manufacture, blue-prints, plating, dyeing, soap compounds, etc.; candy manufacture, foundry, tobacco manufacture, soda fountains, wood bending, water heating, rubber manufacture, stamps, etc.; armature drying, coffee roasting.					
Japanning ovens, drying ovens, melting.					
Soft metal melting.					
Brazing, bending.					
Brazing, hardening, bending.					
Brazing, hardening, bending.					
Brazing, hardening, bending.					
Heating soldering irons.					
Enameling.					
Rivet heating, hardening small parts.					
Melting soft metals, lead and cyanide hardening.					
Melting precious metals, etc.					
Superheating steam, heating air					
To demonstrate boilers					
?					
Melting precious metals. Metal compositions.					
Annealing precious metals. Hardening, annealing					
Annealing precious metals. Hardening, annealing					
Brazing, heating to harden, bending, drop forging					
Brazing, heating to harden, bending, drop forging					
Tempering steel.					
Heating to harden, annealing, case hardening.					
Heating to harden, annealing, case hardening.					
Rivet heating.					
Enameling, hardening, tempering.					
Heating to harden—case hardening.					
Lead hardening, cyanide hardening, metal melting.					
Lead hardening, cyanide hardening, metal melting.					
Enameling, hardening, tempering.					
Soft metal melting.					
Soft metal melting, oil tempering, sweep reducing.					



No. ON PLAN	TRADE No.	KIND OF APPLIANCE	Max. gas consump- tion per hr. cu. ft.	Practical range of working temperature ° F.	SOME USES (NOT ALL) BURNERS
23	2	Brazing table	100	200 to 2000	Brazing, bending, hardening.
24	Model C	10 gallon glue heater	35	150	Glue, wax, compounds.
26	Model C	Height 2 japanning oven	150	120 to 800	
25	3 A	Clothes pressing machine	50		
27	046	Japanning oven	125	120 to 800	Japanning, lacquering, drying.
4	4	Incinerator	120		Garbage, sweep reducing.
29	6	China kiln	360	1000 to 2000	China firing, silver deposit.
30		95 gallon cauldron furnace	150	200 to 800	Water heating, syrups, potash, general boiling.
31	F. 503	Cauldron furnace with pump and agitator	800	200 to 800	Water heating, syrups, potash, general boiling.
32	R. 590	Butcher's boiler	90	200 to 212	General boiling.
33		Sawdust drier	70	150 to 212	Cleaning metal parts.
34	1052	Laundry stove	80		General boiling.
35	F. 7	Rect. cyanide furnace with hood	60	1000 to 1800	Tempering, cyanide hardening, lead hardening.
36	G. 4	Crucible furnace	210	1000 to 2000	Metal melting.
37	E. 4	Lead hardening furnace with hood	135	1000 to 1800	Lead hardening, cyanide hardening.
38	649	Wagon tire heater	500	1200	Expanding tires.
39	C. 9	Semi-muffle furnace	280	1000 to 2000	Hardening and case hardening, tempering.
40	D. 9	Muffle furnace	280	1000 to 1700	Enameling, hardening, tempering.
41	A. 4	Forge	250	1000 to 2500	Heating to harden, brazing, bending.
42	312	Root's acme blower			
43	Type G				
48	304	3/4 H. P. Diehl motor automobile tire vulcanizer	250	200 to 300	Re-treading auto tires
49	13704	6 H. P. gas engine	120		
50	325706	7 1/2 H. P. motor			
51	2	Positive pressure blower			
52	F	Positive pressure blower			
53	29	Automatic heating machine	400	1000 to 1700	Heating to harden, annealing.
54	26	Automatic heating machine	60	300 to 1000	Tempering, bluing.
55	8	Automatic heating machine	300	1000 to 1700	Heating to harden.
56		Clay annealer	75	200 to 250	Boiling out for jewelers.
57		Salt water bath			
58		Oil bath			Hardening baths.
59		Fresh water bath			
43	0	Style C water sterilizer	5	212	Sterilizing water.
44	331	Confectioner's furnace fan blower	250	150 to 400	Candy, syrups, etc.
45	635	Confectioner's air			
		Confectioner's furnace positive pressure	360	150 to 400	Candy, syrups, etc.
46	330	Confectioner's furnace	300	150 to 400	Candy, syrups, etc.
47	695	Confectioner's furnace	135	150 to 400	Candy, syrups, etc.
Out 60	650	Automobile tire heater	1300 (at)	1200	Expanding tires (steel bands).

(a) Gas consumption given is maximum and not operating consumption.

## APPLIANCES ACTUALLY INSTALLED

APPLIANCE	BUSINESS	1913 Consumption cu. ft.
Mould drying oven and crucible furnace	Jewelry manufacture	
Indirect heated oven	Jewelry " drying	594,300
Annealing oven	Lacquers	
4 HP boiler	Brass goods manufacture	839,700
Direct heated oven mould drying	Feather "	273,900
Steam plating box	Bronze goods	2,172,300
1 HP boiler	Dress plating, etc.	203,700
9 HP boiler	Clothing manufacture	493,900
5 HP boiler	Hat	984,500
1 ton coal stereotype melting furnace converted to gas	Silversmiths	589,900
Furnace, forge and vulcanizer	Newspaper	875,200
Soft metal furnace	Artificial limbs	763,300
Tire heater	Electrotypes	472,800
Oven furnace—oil tempering	Wagon repair—stable of department store	55,200
Water still	Hack saw blade manufacture	135,400
Glass firing kilns	Carbonated waters	21,900
Wood drying oven and glue heater	Glass stainers and enamels	33,500
Indirect heated japanning oven	Woodworkers—marquetry	126,500
Glass annealing oven	Platers and japanners	596,000
Tire heater	Thermos bottle manufacture	1,700,900
Air blast gas furnaces	Auto and wagon wheel manufacture	541,000
Oven furnaces	Case hardening, engravers' steel plates	33,000
Air blast gas furnaces	Lava tip manufacture	654,000
Gas ovens for drying raw silks	Electrical novelties	9,229,600
100 gallon cauldron	Silk testing	1,599,200
Steel muffle china kiln	Syrup manufacture	369,500
Melting furnaces for gold	China ware, etc.	1,118,500
Assay furnaces	Assaying	
Burners for distillation	See No. 46	
Water still	See No. 46	
	See No. 46	4,251,100

power field. Where the gas engine is used as the prime mover for manufacturing electricity, all phases of light, heat, and power in all industrial industries are competitively open to the artificial gas industry.

The electric system of lighting has superseded gas lighting in many cases because electric lighting units may be conveniently located as required and be still controlled from a distant convenient point with ease and yet no great care must be exercised to provide against local overheating as in case of gas lighting.

Notwithstanding this disadvantage the incandescent gas light is better than electric light in many circumstances and more often so than is generally realized, in the home the factory and the office; distant control of gas is now used and will shortly be perfected for gas lighting, with all the safety desirable; the pilot light is very satisfactory with the ordinary hand control in single fixtures.



FIG. 4.—GAS LABORATORY. GENERAL VIEW

For power purposes gas used in the gas engine is an active competitor as against the steam engine, but must be used with a belt drive when applied to a multiplicity of machines unless used to drive an electric generator.

In domestic apartment cooking, gas has already displaced coal and is likewise rapidly driving coal from use in private houses and hotel and restaurant work. The gas industry does not fear the invasion

of electricity in this field, and even in the fireless cooker field gas is developing types that will meet any probable electrical developments in sight.

In house and office heating, gas is constantly advancing and with the increase of manufacture of gas from bituminous coal large quantities of gas house

mantle lighting, and (2) surface combustion which greatly increases the efficiency of gas used in heating.



FIG. 5 JAPANING OVENS, CORE DRYING, INCINERATOR, CHINA KILN

coke will come on the market, which, with gas as an auxiliary heating agent, will reduce the use of mined coal in cities.

For general industrial uses, including domestic and industrial laundry purposes, gas is progressing very rapidly as will be shown later.

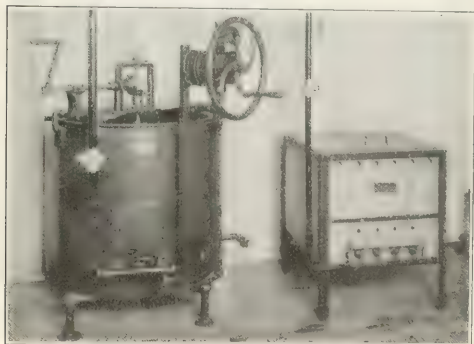


FIG. 6 CAULDRON FURNACE, BUTCHER'S FURNACE

Two interesting developments are attracting the attention of all engineers and give promise of wide application; both require combustion under greater pressures than are common in street distribution to-day: (1) High pressure lighting in which the efficiency is double the present ordinary incandescent



FIG. 7 OVEN FURNACES AND RIVET HEATERS



FIG. 8 FORGES, ANNEALING AND MELTING FURNACES

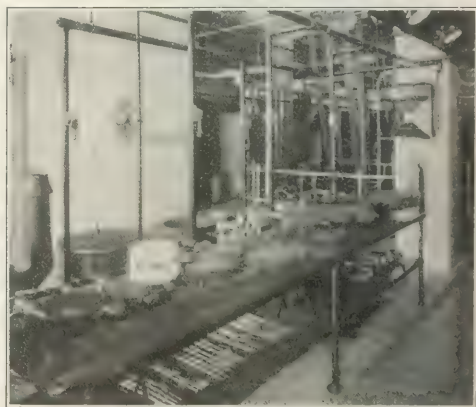


FIG. 9 ASSORTED BURNERS AND BLOW TORCHES

cooking and the industrial appliances where radiant heat will be of value.

High pressure gas lighting may be seen outside of many of the gas offices; good examples may be noted at 16th Street and 4th Avenue, and 41st and 42nd Streets, West of 6th Avenue, New York City.

It is quite within the range of practical dreams to foresee gas supplying heat for hot water, cooking and industrial operations in summer; heating of living spaces in spring and fall and auxiliary to gas house

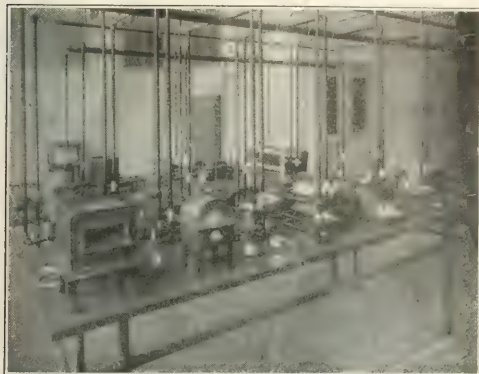


FIG. 10—SOLDERING IRON, MUFFLE, MELTING, ETC



FIG. 13—ELECTROTYPES, SOFT METAL FURNACE

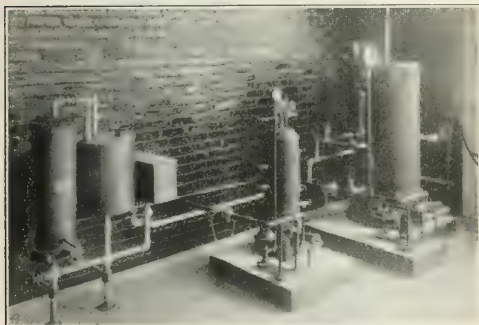


FIG. 11 FEATHER STEAMER, STEAM GENERATORS

coke burned in low pressure boilers in winter. Electricity will supply power for elevator and power use and for lighting, where gas is not so easily applicable, though gas for lighting and power may be found most valuable under certain circumstances.

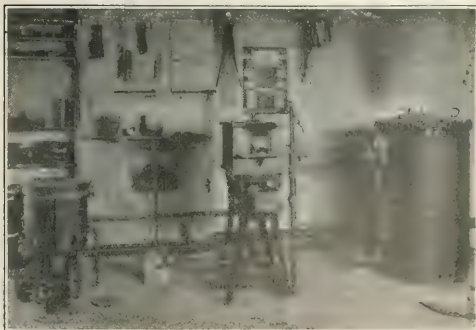


FIG. 12 ARTIFICIAL LIMBS MELTING FURNACE, FORGE, GAS STEAM VULCANIZER

Surface combustion to my mind has most fascinating possibilities to-day. The problem is one of development of design and application to present uses.



FIG. 14 HACK SAW BLADES OIL TEMPERING OVEN FURNACE

It is being recognized that the electrical and gas engineers should work together harmoniously to produce the best results in giving the most efficient service to the public. It follows as an essential



element that the recent pernicious practice of leaving gas pipes out of buildings must be combatted and architects convinced that their clients' interests are sacrificed by so doing.

The new office building of the Consolidated Gas Company located at 15th Street and Irving Place covers an area of 300 by 84 feet, is nineteen stories

well as the day and night outputs in July and December, 1909 and 1913.

A number of examples of sales of gas have been selected from special industries showing the annual

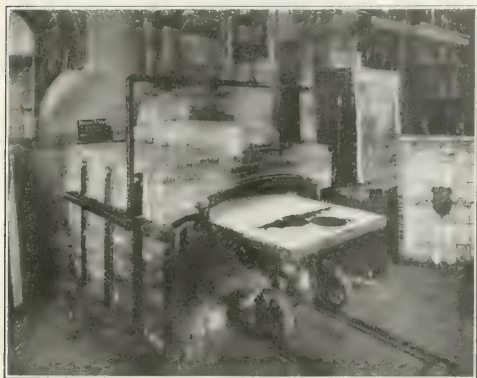


FIG. 15—GLASS FIRING KILN

in height and is completely equipped for both gas and electric lighting; the gas pipes are tested to carry many pounds per sq. in. as against the present street pressure of about  $1\frac{1}{2}$  lb. per sq. in. No products for light, heat and power will be used save those supplied by the central stations of either the gas or electric industry. This building, when completed in all its parts, will be well worth attention as all types of gas



FIG. 16—INDIRECT HEATED JAPANING OVEN

appliances for every conceivable use will be displayed.

It is interesting to note the growth of the gas business over a period of years.

Fig. 1 shows the relative total 12 months output of gas in 1903, 1909 and 1913, as well as of the day and night outputs in 1909 and 1913. It also shows the total December and July output in 1903 and 1913, as

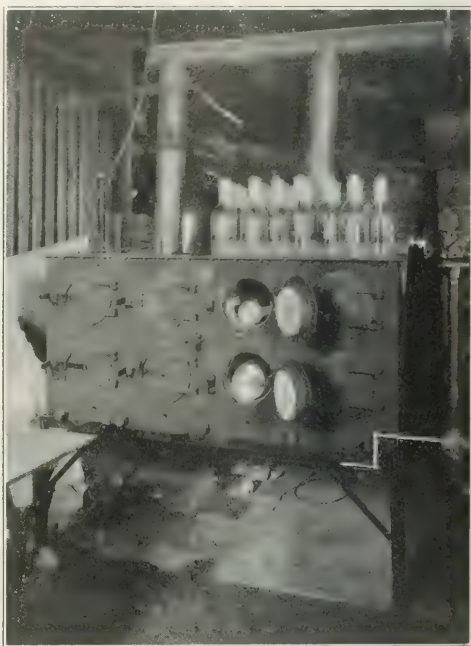


FIG. 17 GLASS ANNEALING OVEN. THERMOS BOTTLES

as well as December and July sales. One is largely for illuminating purposes, while the remainder are fuel users largely. It will be noted that the peak load is not always in December as was formerly the case when the sales were for illumination only.



FIG. 18 RAW SILK DRYING OVENS. SILK TESTING

All branch gas offices have on display many gas burning devices. At Madison Avenue and 42nd Street (New York) will be found a model apartment as well as a large line of domestic and industrial appliances.

At 2nd Avenue and 22nd Street is shown a practical working experimental laboratory for public use. The gas company invites any consumer to bring to this laboratory materials for treatment in any appliance suitable, with electricity and gas furnished free of charge for experimental use, and instruments for careful measurements. Figs. 3-10 give a good idea of this useful aid to the chemist and practical operator and manufacturer.

A table (referred to Fig. 3) of all the appliances in the laboratory, listing the trade number, the name of appliance, the maximum, but not working, gas burning capacity, the range of working temperatures in practical use and some of the uses for which the appliance is now in service. This table is made up for practical every-day reference with the hope that

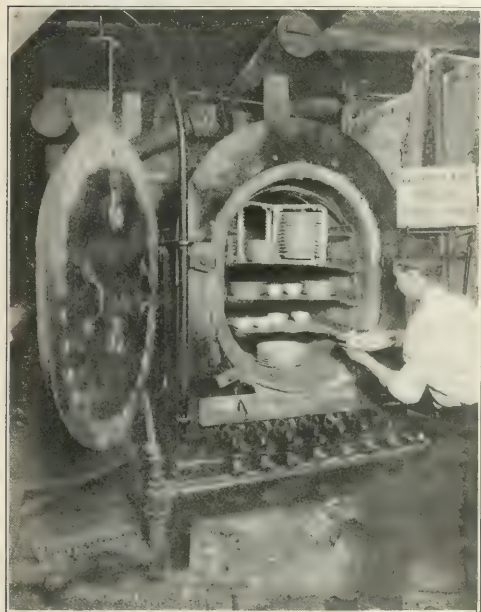


FIG. 19 STEEL MUFFLE CHINA KILN

it may be of use in selecting possible appliances for operations that may be profitably performed by gas as the heating agent.

The maximum hourly gas capacity varies from 5 cu. ft. to 1300 cu. ft. and the working temperatures from 120° to 2800° F. Higher temperatures are attainable if desired.

The gas engineer no longer assumes that gas cannot be economically used in place of coal for the reason that on a unit cost basis gas has a heavy handicap to overcome when compared with coal on a heat unit basis.

From the point of view of heat units only, no one would suppose that a gas-fired steam boiler could be economically used, yet they are being used by scores. Elimination of dirt and hard labor, preparedness for

an uncertain or irregular demand for manufactured product, immediate answer to sudden maximum demand, absolute uniformity of temperature within a wide range, in fact flexibility to a degree, make gas a



FIG. 20—U. S. ASSAY, ASSAY FURNACES

most desirable agent for the manufacturing chemist and industrial manufacturer as well as all engaged in food preparation in domestic, restaurant and hotel service.

4 IRVING PLACE, NEW YORK

#### A SIMPLE EXTRACTION APPARATUS

Stand and Condenser by PERCY H. WALKER<sup>1</sup>

Flask by LORIN H. BAILEY<sup>2</sup>

Received February 20, 1914

A simple apparatus has been designed in the Bureau of Chemistry for general extraction work.

The condenser proper is of the coil metal tube type, originally designed by G. T. Cottle, but generally known as the Underwriters' Laboratories model,<sup>3</sup> modified by lengthening the inlet tube and lengthening and bending the outlet tube, so that the condenser forms a syphon. The stand for supporting the condensers is made entirely of metal and is without clamps. Fig. 1 shows this stand. A is the feed water pipe; the water passes through the pipes B and C; a plug, D, closes the end of C; to each of the cocks E is soldered a 1/8-inch copper pipe, bent as shown, to serve as a water inlet for an individual condenser; the main drain pipe F has an outlet to the sink at H, and is plugged at I; the vertical tubes G, which act as supports and at the same time drain the individual condensers, should have an inside diameter of not less than 1/2 inch.

The condenser and stand may be used with practically any type of continuous extraction. Fig. 2 shows several home-made condensers of this type, adapted to various forms of extractors, the whole battery being heated by an electric hot plate. Beginning at the left we have: (1) an apparatus having a Soxhlet syphon with Knorr flask and mercury seal; (2) a conical flask with a Gooch crucible hung to the coil; (3) a flask with a flattened constriction at the bottom of the neck and an alundum thimble; (4) a

<sup>1</sup> Chief, Contracts Laboratory, Bureau of Chemistry.

<sup>2</sup> Assistant Chemist, Plant Chemistry Laboratory, Bureau of Chemistry.

<sup>3</sup> THIS JOURNAL, 4 (1912), 535 and 856.

flask holding a 25 cc. Gooch crucible (this is much the most convenient form—see Fig. 5 with description); and (5) a condenser alone as it hangs on the drain pipe when not in use, the extreme right space showing the inlet and outlet tubes without any condenser.

The all-metal condenser is strong and inexpensive and can be used for almost all extraction work. While various sizes may be used, it is believed the following specification, which is being used by the Bureau of Chemistry, will prove satisfactory for general work.

SPECIFICATION FOR METAL EXTRACTION  
APPARATUS CONDENSER

The condenser is to be made entirely of copper, nickel-plated, in accordance with the dimensions indi-

Where it is necessary or desirable to avoid contact of metal with the solvent, a glass condenser may be adapted to the stand by the use of one straight and one bent copper tube and a rubber stopper, which can be securely fastened with wire, the specifications for such a glass condenser being as follows:

SPECIFICATIONS FOR GLASS INSIDE CONDENSER

To be made entirely of well annealed glass as per dimensions given in the accompanying drawing (Fig. 4), the neck to be  $1\frac{1}{2}$ " long and 1" inside diameter, with the opening slightly flanged to take a cork securely; the bulb (B) to be from  $2\frac{1}{2}$ " to  $2\frac{3}{4}$ " diameter; the barrel (C) to be from  $2\frac{1}{2}$ " long to  $2\frac{3}{4}$ " and not less

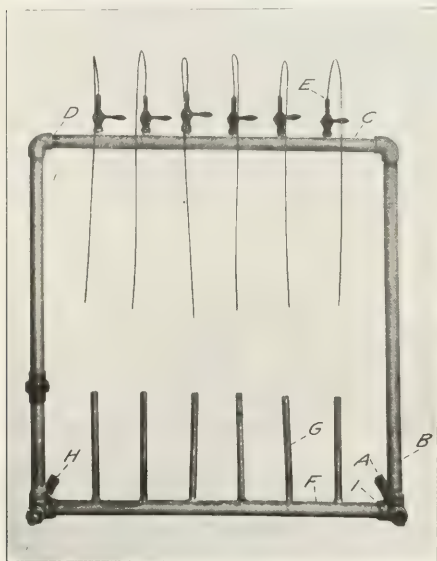


FIG. 1—STAND FOR SUPPORT OF CONDENSERS

cated on the accompanying drawing (Fig. 3). The parts indicated on the drawing as (a), (b), (c), (d) and (e) are to be one continuous piece of tubing,  $\frac{1}{4}$ " inside diameter with walls  $\frac{1}{32}$ " thick. The coil (b) is to be from  $1\frac{3}{8}$ " to  $1\frac{1}{16}$ " outside diameter, and from  $2\frac{3}{4}$ " to 3" long from the top of the plate (f) to the bottom of the coil, and to have not less than four complete turns. The cover (f) is to be one piece of metal,  $\frac{1}{32}$ " in thickness and  $2\frac{1}{2}$ " in diameter, turned down at the margin to form a vertical flange  $\frac{3}{8}$ " high. The cover is to be brazed to the inlet and outlet tubes in vapor-tight joints. The tubes (a) and (c) must meet the cover at right angles, and the coil (b) must be concentric with the cover (f).

Necessary conditions for acceptance shall be:

(1) That water shall circulate freely through the continuous tubing and coil.

(2) That the coil shall enter, without bending, a tube of  $1\frac{1}{16}$ " inside diameter.

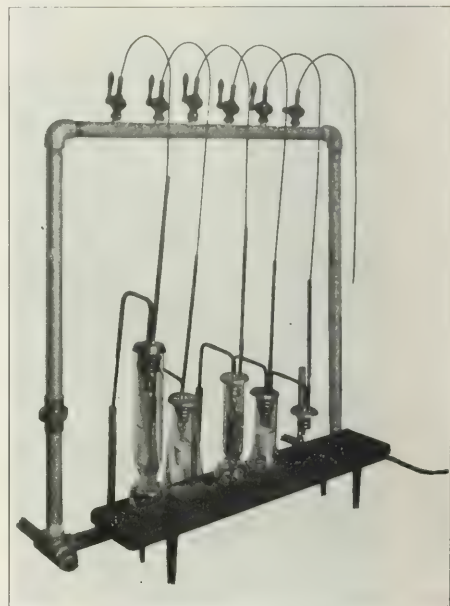


FIG. 2—HOME MADE CONDENSERS ADAPTED TO VARIOUS FORMS OF EXTRACTION APPARATUS

than  $1\frac{1}{4}$ " nor more than  $1\frac{3}{8}$ " outside diameter, with a hook (D) about  $\frac{1}{4}$ " long at the lower end; the flange (E) to be about  $2\frac{1}{2}$ " in diameter, and  $\frac{1}{4}$ " deep, sealed to bulb (B) near its outer extremity, and concentric with (A) and (C).

Fig. 5 shows the type of extraction flask, mentioned above, which accommodates either a small siphon tube or a 25 cc. porcelain Gooch crucible. The tube or crucible is held in position by the inward projections in the side of the flask. When the extraction is completed the tube or Gooch crucible may be removed, a solid crucible inserted, and the solvent thus recovered. The flask is made according to the following specifications.

SPECIFICATIONS FOR EXTRACTION FLASK

To be made of good glass, well annealed. Height of flask 130 mm., inside diameter of top from 39 to 41



mm., outside diameter at base from 50 to 56 mm., flask to have 3 equi-distant inward projections, made to touch the circumference of a circle 27 mm. (26 to 28 mm.) in diameter and concentric with the sides of the flask, points of projection to be 30 mm. (29 to 31 mm.)

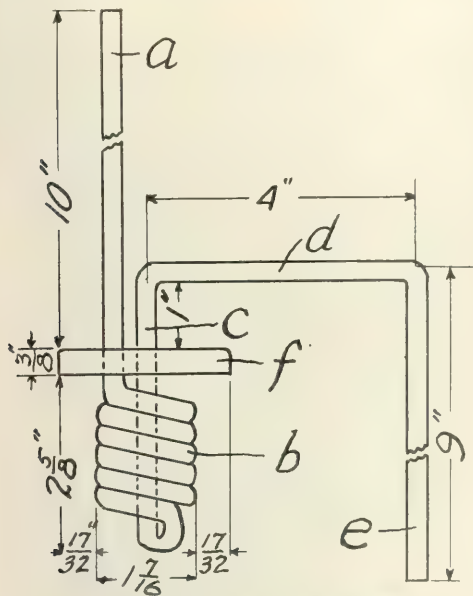


FIG. 3—METAL EXTRACTION APPARATUS CONDENSER

above base. Enlargement of cylinder to form base to begin immediately below projections; bottom to be entirely flat with rounded edge, top made smooth and parallel to base, flask to be of approximately uniform thickness throughout; weight of the flask to be from 40 to 50 grams.

The advantages of this apparatus are: (1) the stand

offers a rigid support for the condenser at all times, without the use of the clamps; (2) a cheap, durable and efficient condenser, which may be adapted to practically any form of continuous extraction apparatus; (3) the elimination of all rubber, corks, ground glass,

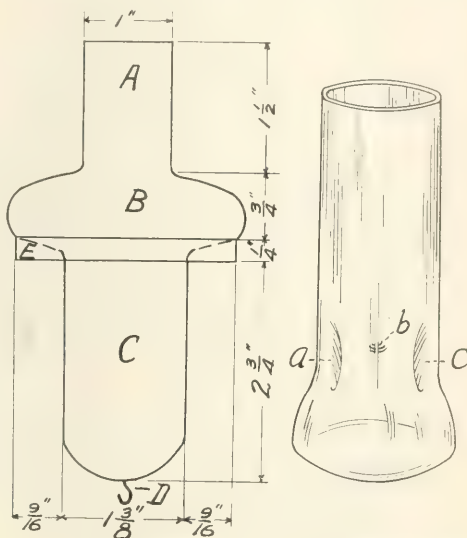


FIG. 4—GLASS INSIDE CONDENSER

FIG. 5—EXTRACTION FLASK WHICH ACCOMMODATES A 25 CC. GOOCH CRUCIBLE

or mercury seal connections; (4) extractions may be safely run over night, since there is practically no danger of breakage due to change in water pressure; (5) the flask is light enough to be accurately weighed, can be easily cleaned, and is of such a form that all of the extract can be transferred.

BUREAU OF CHEMISTRY, DEPARTMENT OF AGRICULTURE  
WASHINGTON

## ADDRESSES

### RECENT IMPROVEMENTS IN GAS MANUFACTURE<sup>1</sup>

By ALFRED E. FORSTALL

Understanding it to be intended that I should cover only the manufacture of illuminating gas in central station plants I have limited myself to this phase of the general subject of gas manufacture.

The process of manufacturing illuminating gas divides itself into two stages, the generation of crude gas from the raw materials, and the purification of this crude gas in order to make it fit for general use.

#### GENERATION OF CRUDE GAS FROM RAW MATERIALS

Taking up first the generation of coal gas, an important recent improvement has been the development and quite general installation of retorts set vertically, which were unsuccessfully experimented with in the early years of the nineteenth century. Retorts set horizontally were, however, finally adopted and used solely, until, in 1885, M. Andre Coze developed a setting in which

<sup>1</sup> Read before the New York Section of the Society of Chemical Industry, The Chemists' Club, New York, March 27, 1914.

the retorts were inclined at an angle of from 29° to 33° to the horizontal. At such angles the coal would spread fairly evenly over the whole length of the retort by gravitation and the coke would run out fairly easily when the charges were thoroughly carbonized. Though adopted quite generally on the Continent of Europe and in Great Britain only three important installations of inclined retorts, and not more than five or six minor ones, were made in the United States.

#### VERTICAL RETORT SETTINGS

In the year 1902 two different types of vertical retort settings, the intermittent and the continuous, were brought to the attention of gas men. The intermittent type, in which an amount of coal which nearly or entirely fills the retort is dropped in at one time and allowed to remain until completely carbonized, when the resulting coke is dropped out, also at one operation, was developed by Dr. Bueb of the German Continental Gas Company in the gas works at Dessau, Germany.

#### INTERMITTENT VERTICAL RETORTS—DESSAU<sup>2</sup>

The first patent taken out for these retorts, in the early part of

1902, described them as provided with outlets, spaced from top to bottom along the whole length of the retort and opening into a vertical flue so placed in the setting as not to be exposed to a high heat, the object being to permit the gas as it was driven out of the coal to escape to the hydraulic main without being subjected to contact with either the highly heated coke or the walls of the retort. Settings built under this patent were put into operation in 1903 but the side outlets were abandoned soon after actual operation began, and by 1905 the design had been developed to that which is now being employed, in which the gas evolved from each portion of the charge travels through all the superincumbent portions, before it escapes to the hydraulic main.

As the Dessau verticals have been developed in Europe the retorts are made either four meters or five meters (13 ft. 2 in. or 16 ft. 5 in.) long with cross-sectional dimensions of approximately 9 in. by 22 in. at the top and 14 in. by 27 in. at the bottom and are set in groups of either twelve or eighteen, each group being heated by its own gas producer, or generator furnace, and provided with its own recuperators. In the only installation of this type in the United States, which is at Providence, R. I., the retorts are 13 ft. 2 in. long with the same cross-section as given above and are set ten in a bench. The coal is charged into the retorts from overhead bunkers and the coke is dropped into buggies or into a conveyor.

The combustion of the producer gas takes place in a combustion chamber surrounding the lower ends of the retorts and the hot products of combustion pass horizontally to the back of the setting and then up to a second set of horizontal flues running to the front, up again to a third set of horizontal flues running to the back and then into a fourth set of flues running to the front and pass out from the top of the bench to the recuperators and thence to the chimney.

#### INTERMITTENT VERTICAL RETORTS—UNITED GAS IMPROVEMENT CO.

In the United States the United Gas Improvement Company began experimenting with intermittently filled vertical retorts about 1908. As a result of these experiments the benches of this type last built contain nine retorts each 18 ft. 6 in. long with an oval section 12 in. by 22 in. at the top and 18 in. by 30 in. at the bottom. The reasons given for the use of the larger cross-section are that when it was smaller the coal coked too rapidly at the top of the retort causing excessive pressure at the bottom, that with the small retort the discharge of the coke did not take place satisfactorily except when the whole charge of coal was thoroughly carbonized, while a large retort will discharge readily even when the coal has not been thoroughly carbonized, and that the larger retorts produce larger coke, an advantage in many localities.

In this type of setting the combustion of the producer gas also takes place around the lower ends of the retorts and the products of combustion pass upward to the top of the setting.

The German practice is to fill the retorts completely with coal while the United Gas Improvement Company leave 4 ft. of the retort at the top empty, to provide a space in which the heavy hydrocarbon vapors may be converted into gas by the action of radiant heat.

It is interesting to note that in 1880 Mr. C. F. Dietrich obtained a United States patent making claims for a setting of retorts which were very similar to those of the original Bueb patent, including even the lateral openings into a channel protected from heat through which the gas could pass out from the retort. At that time, however, conditions in this country were favorable to the manufacture of carbureted water gas and the field for coal gas did not seem to warrant the trouble of developing a new method of manufacture, so that apart from building one experimental bench nothing was done by Mr. Dietrich to develop these retorts.

#### PASSAGE OF GAS THROUGH INTERMITTENT RETORTS

The reason for the provision of side outlets in the retorts under the original Bueb patent was the belief that, if compelled to pass up through the incandescent charge, the hydrocarbons first evolved from the coal would be over-decomposed into hydrocarbons of lesser worth from the illuminating and calorific value standpoint, and that carbon and naphthalene would be formed and cause trouble during the handling of the gas as it passed from the generating apparatus to the consumer. The disadvantage of the side outlets was that the retort could not be heated around its entire perimeter and that therefore more fuel was required for the carbonization of a given weight of coal than where the heat could be applied around the entire perimeter. When the lateral outlets were bricked up and the gas taken off from the top of the retort the decomposition of the hydrocarbons was not as great as had been anticipated, provided the retorts were heated to a very high temperature and care taken to completely fill them with coal. It was claimed that under these conditions the generation of gas from the portions of the coal in contact with the internal surfaces of the retorts was rapid, owing to the high heat, and this coal was at once converted into a compact coke, impermeable to the gas generated. The gas was therefore forced to pass, from all points of the layer in which carbonization was taking place, inward and upward through the uncoked and more permeable portions of the charge. Its temperature was thus prevented from rising beyond the point at which over-decomposition of the heavy hydrocarbons, with the formation of carbon and naphthalene, would take place.

This theory as to the course followed by the gas in passing through the charge in an intermittently charged vertical retort was for a long time accepted as correct, but recently Dr. H. L. Colman, in England, and Mr. O. B. Evans, in the United States, have reached the conclusion, as the result of experiments, that in reality only part of the gas travels through the core of uncarbonized coal and the rest passes through the incandescent coke.

Dr. Colman argues that if even the largest portion of it traveled through the uncarbonized coal, the gas would show some of the characteristics of a gas produced at a low temperature, modified to a certain extent by the gas produced in the latter stages as the temperature of the coke is raised, and that the tar produced would be a low-temperature tar containing but a small amount of aromatic substances. As a matter of fact his analyses had shown that the gas possessed all the characteristics arising from exposure to high temperatures, the proportion of hydrogen to methane being even higher than that obtained from the same coal when distilled in highly heated horizontal retorts, and that the tar produced, although containing more paraffin derivatives than did tar from horizontal retorts, consisted chiefly of aromatic substances, showing that, during its formation, the vapors produced at low temperatures must have been subjected to a considerably higher temperature before passing out from the retort. This could not happen if even the larger part of these vapors passed through the uncarbonized coal, since then the travel would be in a direction which would expose them to a constantly decreasing, instead of to a higher, temperature. Moreover, the existence of a high pressure in the retort at the commencement of carbonization when the area of the core was the greatest and the diminishing of this pressure as carbonization proceeded, although the rate at which gas was produced did not decrease greatly during the first seven hours of the charge, while the area of the core did decrease quite rapidly, was strong evidence that the gas did not find its principal direction of travel through the core. He concludes that the great bulk of the gas is produced on the outer side of the pasty layer formed by the coal as it carbonizes and that this gas mainly travels through the hot coke, mixing with the poorer gas produced by the continued action of heat on the low-temperature

coke first produced. The gas produced on the inner side of the pasty layer will pass through the coal and he considers it probable that the vapors which pass in this direction form the undesirable paraffin constituents of the tar so that as far as travel through the core does take place it is disadvantageous.

Mr. Evans, reasoning from the pressure conditions existing in the interior of an intermittently charged vertical retort, came to the conclusion that during the early part of the charge, when the layer of coke formed around the perimeter of the retort was compact and offered no ready means of passage to the gas, most of the gas produced was obliged to force its way through the pasty layer of coal, in the initial stage of carbonization, and pass up through the uncarbonized coal, but that as the outer layer of coke contracted and cracked under further heating most of the gas formed in the latter portions of the charge passed up through this coke. He also concluded that of the gas made during the first six hours of the charge, which amounted to 70 per cent of the total amount of gas made, 45 per cent passed up inside of the pasty layer through the core and 55 per cent through the hot coke next to the retort walls, and that the gas evolved at low temperatures escapes through the core while that evolved at high temperatures escapes along the wall. Mr. Evans considers that this is advantageous since the low-temperature gas is more subject to injury by undue exposure to heat, and this is correct provided that after leaving the coal this gas is exposed to heat in a free space at the top of the retort.

This discussion as to the path followed by the gas in passing out from intermittently charged vertical retorts has been given somewhat at length because of the claims originally made that the freedom from naphthalene experienced with gas made in such retorts was largely due to the fact that the travel was through the cool core of uncarbonized coal.

#### ENGLISH DEVELOPMENT OF CONTINUOUS VERTICAL RETORTS

While the work of the Germans in connection with vertical retorts was confined entirely to those charged intermittently, in England the design of such settings was approached with the idea of adapting them to continuous carbonization. This had been experimented with in connection with the horizontal retorts and had given good results as far as the quantity and quality of the gas were concerned but had always proved a failure from the manufacturing standpoint because of mechanical troubles.

In 1902 there was built in Exeter a setting of vertical retorts into which the coal, in amounts varying from 2 lbs. to 7 lbs., was charged at regular intervals, the length of which could be varied. The retorts, about 9 ft. long, were made straight for part of the distance and then were curved so that the coke was withdrawn through an opening in the side of the setting at right angles to that in the top through which the coal was charged. The coke was drawn intermittently in comparatively large amounts at one time so that the extent to which the retort was filled with coke and coal undergoing carbonization varied quite considerably. After being tried in several places in England, further use of the settings was abandoned because of trouble experienced with the working of the coal-feeding device and in keeping the curved portion of the retort from cracking, and also with the formation of lampblack owing to the large variation in the volume of the charge because of the intermittent drawing of the coke and the consequent variation in the extent to which the gas passing off from the charge was exposed to heat in the vacant space left at the top of the retort.

#### WOODALL-DUCKHAM VERTICAL RETORTS

While this retort was being experimented with Messrs. Woodall and Duckham were developing at Bournemouth, England, another type of continuously charged and operated vertical

retorts. Starting with a mechanical coal feed as well as mechanical and continuous extraction of the coke, the former was soon abandoned because of operating difficulties and the introduction of coal into the retort is now brought about entirely as a result of the extraction of coke at the bottom. The construction of the coke extractors has also been very materially changed from the form shown in the original patent and the first plant erected.

As now built each retort is surmounted by a charging magazine filled through a rotary valve from an overhead coal bunker and holding enough coal for two hours' supply. There is free communication between the magazine and the top of the retort, the coal in the former being supported by that in the retort. As the coke extractor withdraws the coke from the bottom the whole column of material in the retort settles and coal runs in at the top from the magazine, the supply of coal in which is replenished at intervals of from twenty minutes to an hour.

The coke extracting device consists of a rotating horizontal shaft provided with arms placed spirally around it and of loose arms hung on hinges at their upper end and having sufficient weight to hold back the coke except as their lower ends are pushed out by the action of the revolving shaft. The coke is discharged into a closed hopper which will hold the amount produced during two hours and is intermittently emptied either into dumping wagons running on an industrial railway track, or into a conveyor. The extractor can be run at varying rates of speed to suit the differing amounts of coal that can be carbonized under varying conditions.

As originally built the settings consisted of four oval retorts 25 ft. long and having cross-sectional dimensions of practically 9 in. by 23 in. at the top and 20 in. by 29 in. at the bottom. In recent installations the retorts have been replaced by rectangular ovens, or slots, of the same length and having cross-sectional dimensions of 8 in. by 3 ft. 10 in. at the top and 20 in. by 5 ft. 3 in. at the bottom. At the top of these slots there is a division plate, extending down an adjustable distance, which forms two separate spaces, into one of which the coal magazine opens while the other is kept free from coal so that the gas can pass out through it and in passing out be exposed to radiant heat for the purpose of decomposing the hydrocarbon vapors with low boiling points. As the settings are operated it would seem that the desired effect was obtained to only a very limited extent, if at all.

The combustion of the producer gas begins at the top of the setting and the products of combustion pass down, surrounding the retorts and are taken off into the recuperators a short distance above the bottom. From the recuperators they pass either directly to the chimney or in some cases are taken through the tubes of a waste heat boiler which furnishes practically all the steam required for the operation of the plant.

The primary air is heated before entering the furnace by passing across the setting in contact with the side walls of the retorts at their lower end, and the coke is sufficiently cooled in this way to require no quenching.

#### GLOVER-WEST VERTICAL RETORTS

While Messrs. Woodall and Duckham were developing their design, Messrs. Young and Glover were also doing, at St. Helens, England, work which has resulted in what is now known as the Glover-West system of continuous vertical retorts. The chief differences between the Woodall-Duckham and the Glover-West systems are in the form of the coke extractor and in the methods of heating the retorts. In the Glover-West, as in the Woodall-Duckham, coal runs into the retorts, from a charging magazine in free communication with the top, as the coke is extracted at the bottom. The coke extractor is in the form of a worm set with its axis vertical and slowly revolved, and delivers coke into a receiving chamber, large enough to hold that produced during a period of two hours and regularly discharged



at intervals of any length less than two hours. The retorts are oval in section and have a total length of 20 ft. with cross-sectional dimensions of 10 in. by 30 in. at the top and 22 in. by 36 in. at the bottom. To the bottom of each one is added a cast iron chamber 3 ft. deep, at the bottom of which is placed the coke extractor. The retorts are set in groups of eight and the setting is divided into either two or four chambers so that the retorts can be worked in units of four or two. The combustion of the producer gas takes place at six points evenly spaced along the portion of each chamber extending from the bottom to within about 5 ft. of the top, and the products of combustion, after passing horizontally around each set of retorts, ascend through vertical flues to chambers surrounding the upper 5 ft. of the retorts, from which they pass to the chimney. The secondary air is heated by passing the cast iron chambers at the lower end of the retorts and this cools the hot coke on its way to the coke extractors, and does away with the necessity of quenching it when taken from the coke chambers.

#### OPERATION OF HORIZONTAL RETORTS MODIFIED

Shortly after, and partly as a consequence of, the successful introduction of intermittently charged vertical retorts the method of operating horizontal retorts was substantially modified. This had been to charge such retorts with a layer of coal about 4 in. to 5 in. thick leaving a large free space above the coal, through which the gas passed to the mouthpiece and standpipe. The maximum charge for each of the 9 ft. retorts with one end permanently closed, in general use in the United States, was from 340 lbs. to 350 lbs. of coal. The front end of the retort being enclosed in the front wall of the bench for a depth of 13 in., almost a foot of the length was not effective for carbonizing purposes and the weight of charge was not more than 45 lbs. and in many cases not over 40 lbs. per lineal foot of the effective portion. There had been some theoretical discussion of the advisability of more completely filling the retorts, but this had not produced any result in practice until the completely filled vertical retorts afforded an object lesson of the freedom from carbon and naphthalene troubles secured by reducing the extent to which gas was exposed to contact with the highly heated walls of a retort. In England, where the use of through retorts, or those open at both ends, was common, it was easy to change from the lighter charges to the heavier ones, but in the United States it was necessary to change to the use of through retorts instead of single end ones before the increase in weight of charge could be made, since where the coke must be drawn from the retort by means of a rake it is necessary to leave sufficient space above the charge to permit the free passage of the rake, while with the through retorts, from which the coke can be pushed, provision for the passage of the rake does not have to be made. The present practice, where through retorts are in use, is to charge about 70 lbs. of coal per lineal foot of the effective portion of the retort. When so charged from 66 per cent to 70 per cent of the area of the retort is occupied by coal leaving only 30 per cent to 34 per cent of the area for the passage of the gas, while when weighing 40 lbs. to 45 lbs. per lineal foot of retort the charge only occupies from 30 per cent to 36 per cent of the area. The expansion of the charge during the coking process makes the actual free space left in the retort still smaller in proportion for the heavy charges.

The use of heavier charges has resulted in a large increase in the amount of gas made per pound of coal with a decrease in the operating difficulties caused by the presence of free carbon in the gas and in the tar. In England the yield of gas, which formerly averaged only about 10,500 cu. ft. per ton of 2240 lbs. of coal now averages nearly 12,000 cu. ft., while in one plant in the United States, that at Worcester, Mass., the former average yield of 5 cu. ft. per pound has been increased to 5.9 cu. ft. In other works in the United States which have adopted the heavy charges the yields of gas have been increased about 10

per cent as compared with those formerly obtained. This increase in yield has not been accompanied by a decrease either in the illuminating value or in the calorific value per cubic foot and has therefore resulted in obtaining a greater total illuminating value and calorific value in the gas from a given quantity of coal.

The yield from the continuous vertical retorts is also greater than that formerly obtained from horizontal retorts operated with light charges, but in this country has not been as large as that obtained from the horizontal retorts at Worcester, Mass.

#### COMPARISON OF GASES FROM HORIZONTAL AND VERTICAL RETORTS

Some analyses have been obtained of the gas made in each of two plants, one having horizontal retorts and the other vertical retorts of the Woodall-Duckham type. The horizontal retorts are operated with moderately heavy charges which, however, do not come up to 70 lbs. per lineal foot of retort. These plants are under the same management and the coal used is purchased from the same company and is presumably practically the same, so that the analyses show, to some extent, the difference in the gas due to the difference in method of carbonization.

	Horizontal retorts Per cent	Vertical retorts Per cent
Carbon dioxide.....	1.44	1.49
Benzol.....	0.67	0.55
Illuminants.....	3.15	3.98
Oxygen.....	0.48	0.28
Carbon monoxide.....	4.75	6.90
Hydrogen.....	51.36	45.02
Methane.....	33.60	37.33
Nitrogen.....	4.55	4.44
Candle power (Sugg D burner).....	100.00	99.99
Calorific value (B. t. u. per cu. ft. by calculation).....	13.60	15.57
Calorific value (B. t. u. per cu. ft. observed).....	610.00	
Yield, cu. ft. per pound of coal.....	4.85	615.00 5.39

The total illuminants run slightly higher, and there is much less hydrogen in proportion to the methane, in the gas from the vertical retorts than in that from the horizontal retorts. The illuminating value of the gas from the vertical retorts is also higher while the yield per pound of coal was 10 per cent higher. During the period over which the analyses of the gas from the horizontal retorts were taken, very wet coal was being carbonized and this may have affected the illuminating value and the yield of gas which were lower during this period than the average for the preceding month, but even the averages for that month were lower than the results obtained from the vertical retorts which, however, were those made during a test lasting eight days and in regular working the results have not been quite as good.

Comparable analyses of the gas made in the working scale testing plant at the gas works in Birmingham, England, both in intermittent vertical retorts, of the Dessau type but apparently charged so as to leave a free space above the coal at the top of the retort, and in horizontal retorts have been given by Dr. W. B. Davidson as follows:

	Dessau Verticals Per cent	Horizontals Per cent
CO <sub>2</sub> .....	2.4	2.2
C <sub>2</sub> H <sub>6</sub> .....	2.8	3.4
CH <sub>4</sub> .....	0.5	0.5
CO.....	10.3	9.7
CH <sub>4</sub> .....	28.0	31.5
H <sub>2</sub> .....	51.0	47.3
N <sub>2</sub> .....	5.0	5.4
Illuminating value, candles.....	100.0	100.0
Net calorific B. t. u. per cu. ft.....	15.0	18.0
	500.0	525.0

NOTE.—The illuminating values given by Dr. Davidson cannot be compared directly with those given previously since they were obtained from the Metropolitan No. 2 Argand burner and are probably about three candles higher than would have been obtained had the Sugg D Argand been used as was done in the other case.

Dr. Davidson observes that the gas made in the vertical retorts is deficient in unsaturated hydrocarbons and methane and high in hydrogen, and that a cursory examination of the analyses

leads to the conclusion that the hydrocarbon gases are subject to more drastic degradation before leaving the retort in the vertical system than they are in the horizontal system, but that it is not unlikely that the gas suffers both in quality and volume by the escape uncracked of a larger proportion than usual of tar oil vapors.

Experience with the United Gas Improvement Company verticals operated with a large free space above the coal seems to show that the provision of this free space leads to an improvement in the illuminating and calorific value of the gas, which is obtained at the expense of the extra quantity of tar produced when the retorts are completely filled according to the strict use of the Dessau system.

As far as the quality and quantity of the gas are concerned intermittent vertical retorts of the Dessau system give poorer results than are obtained in horizontal retorts, while the intermittent verticals of the United Gas Improvement Company type and the continuous verticals do not give any better results along these lines than can be obtained from properly operated horizontal retorts. The improvements effected by the use of vertical retorts consist in a saving of labor in medium-sized plants in which it is impossible to work charging and discharging machinery for horizontal retorts to advantage, and in greater freedom from trouble caused by free carbon and naphthalene, while the sulfur compounds other than sulfureted hydrogen are also produced in smaller amount. In addition there is a saving in the ground space required although it is necessary to go higher into the air with verticals. To these advantages the continuous vertical retort system adds that of practically complete avoidance of the smoke and steam emitted during the charging and discharging of either horizontal retorts or intermittent vertical ones.

#### SUGGESTED METHOD OF DISTILLATION OF COAL

The work recently done in determining the character of the products given off by coal subjected to distillation at different temperatures indicates that the greatest efficiency, from the gas-making standpoint, in the carbonization of coal could be obtained by so adjusting the heating of continuous vertical retorts that the temperature of the upper 2 ft. or 3 ft. of the charge should never exceed  $1000^{\circ}$  to  $1100^{\circ}$  F., while that of the lower portion of the charge would be carried as high as  $1800^{\circ}$  F. By this method of heating, the rich hydrocarbons would be driven off from the coal without having to come into contact with very highly heated surfaces while the gas remaining after these hydrocarbons were driven off, which is of such a character as not to suffer to any great extent from such contact, would be entirely expelled from the coal in the lower portion of the retort. In order to decompose the heavy hydrocarbon vapors, which would otherwise condense into tar, in such a manner as to convert them into the maximum amount of permanent gas mixed with hydrocarbon vapors that could be carried by the gas, with the setting free of the minimum amount of carbon, all of the gas leaving the top of the charge should then be passed through a free space exposed to heat radiated from walls carried at a temperature adjusted to the rate of travel of the gas, but probably about  $1400^{\circ}$  to  $1500^{\circ}$  F. This free space could be maintained either in the upper part of the retort or, if this leads to difficulty in feeding the coal, it might be entirely separate from the retort and possibly common to several retorts.

This method of manufacture would increase the quantity and quality of the gas at the expense of the tar and would not be advantageous unless the value of the gas gained was greater than that of the tar lost. It has never been actually worked but in my opinion is entirely feasible.

#### IMPROVEMENTS IN MANUFACTURE OF CARBURETED WATER GAS

The recent improvements in connection with the manufacture of carbureted water gas consist in the devising, and putting into

general use, of appliances for measuring the amount of air blown through the fuel bed during the "blow," or heating-up period, and the amount of steam passed through the fire during the "run," or gas-making period, together with the use of electric pyrometers for indicating the temperatures existing at selected points in the checker brick of the carbureter and superheater of the type of apparatus most commonly employed in the manufacture of this gas. The use of these appliances makes it possible to determine and operate, the apparatus constantly, under the conditions of blast, amount of steam used and temperature to which the oil vapors are subjected which give the best results and by so doing to decrease the amount of fuel used and increase the efficiency of the conversion of the oil into oil gas, as compared with the former more or less hit or miss operation.

#### PREPARATION OF CRUDE GAS FOR DELIVERY TO CONSUMER

In the second division of the process of gas manufacture, that of the preparation of the crude gas for delivery to the consumer, the recent improvements have been chiefly in connection with the removal of hydrogen sulfide and the other sulfur compounds present in the crude gas. For many years attempts have been made to use, for the removal of hydrogen sulfide from coal gas, the ammonia obtained from the gas itself. About 1886 a process for doing this was devised by Claus in Belfast, Ireland. Although chemically correct it proved too complicated mechanically and was finally abandoned largely because it was impossible to keep in working order the numerous pumps required for its operation. It is possible that if modern centrifugal pumps had been available the process might have been successfully operated.

#### AMMONIA FOR REMOVAL OF HYDROGEN SULFIDE

In the United States an extremely simple method of purification of gas from sulfureted hydrogen by means of ammonia has been recently devised by Mr. Jas. G. O'Neill and used on gas produced in coke ovens and sold for illuminating purposes.

The ammonia in ordinary ammoniacal liquor is already largely saturated with sulfur and carbon dioxide and one of the chief problems in connection with the use of this liquor for more complete removal of sulfureted hydrogen is to accomplish its conversion into a condition suitable for combination with sulfureted hydrogen without introducing too much complication of apparatus. Mr. O'Neill has solved this problem in a very simple manner by using liquor withdrawn from the still of the Coffey type, which is in general use in gas works for the concentration of ammoniacal liquor. He finds that when the liquor fed to the still has reached the point at which it has a temperature of  $214^{\circ}$  to  $215^{\circ}$  F. it has lost 80 per cent to 90 per cent of the hydrogen sulfide and 70 per cent to 80 per cent of the carbon dioxide, but still retains practically all the ammonia, which it contained when it entered the still. When brought in contact with crude coal gas in scrubbers of the ordinary type, this liquor can take up on an average 500 grains of hydrogen sulfide per gallon and if used in sufficient quantities will reduce the hydrogen sulfide from as much as 900 grains, down to from 20 to 30 grains, per 100 cu. ft. of gas. If the complete removal of the hydrogen sulfide with liquor is attempted the average efficiency of the liquor is much less than this and it is more economical to use the liquor only to the extent named and then finish the removal of the sulfureted hydrogen by the ordinary process of purification by means of hydrated sesquioxide of iron.

The process devised and used by Mr. O'Neill adds to the apparatus customarily found in gas works only a heat exchanger, in which heat is transferred from the hot liquor coming from the concentrating still to the cool liquor on its way to the still and a cooler for further cooling the treated liquor, both of which are simple and inexpensive. Apparently this process could be adopted in many coal gas works with a saving in the labor re-

quired to operate the oxide of iron purifiers and also in the investment in the purifiers required for a given quantity of gas.

#### REMOVAL OF OTHER SULFUR COMPOUNDS

In Europe, where the gas coals contain as a rule more sulfur than do those in common use in the United States, and on the Pacific Coast, where gas is largely made from crude petroleum containing a somewhat high percentage of sulfur, the problem of reducing the amount of sulfur compounds, other than hydrogen sulfide, contained in crude illuminating gas has had some importance. In those parts of the world, therefore, attention has recently been paid to new methods of removing the principal one of these sulfur compounds, carbon bisulfide.

Of the more recent processes having this object, the one first brought to the attention of gas engineers was that devised by Messrs. Hall and Papst and used since 1908 for the treatment of all the gas made, about 3,000,000 cu. ft. per day, in the works at Portland, Oregon. In this process the gas is merely heated to a temperature of from 1300° to 1600° F. by being passed through tall cylindrical vessels, formed of steel plates lined with fire clay blocks and filled with a checker work of fire brick, which are heated by the combustion in them of fuel oil. The vessels are in pairs, one being in process of heating while gas is being passed through the other. The operations are reversed as soon as the vessel through which the gas is passing becomes cooled below the effective temperature. Under the effect of heat the carbon bisulfide reacts with the water vapor present in the gas and is largely converted into hydrogen sulfide, which is removed by passing the gas through an additional set of purifiers containing oxide of iron.

#### NICKEL CATALYZER FOR DECOMPOSITION OF CARBON BISULFIDE

Another process which has been employed on a large working scale is that devised by Mr. E. V. Evans and used since the beginning of 1913 to treat all the gas made, about 10,000,000 cu. ft. per day, at the works of the South Metropolitan Gas Company, of London. This process utilizes the catalytic effect of nickel in accelerating the reaction between carbon bisulfide and steam, by which hydrogen sulfide is produced and carbon set free. The catalyzer is in the form of balls, presumably of fire clay, 1 in. in diameter impregnated with nickel obtained by the reduction of the chloride in a current of hydrogen. These balls are contained in tubes having a length of 11.5 ft. and a diameter of 6 in., through which the gas to be treated is passed. Before reaching the catalyzing tubes the gas passes through heat exchangers, or recuperators, in which it absorbs heat from the gas passing out from the apparatus, and then through preheating tubes in which its temperature is raised to 750° F. With this preheating of the gas it is possible to carry on the process while maintaining a temperature of 800° F. in the catalyzing tubes and the principal direction in which the process has been gradually improved has been this preheating of the gas before it enters the catalyzers. A single combustion chamber, supplied with producer gas from an outside producer, furnishes the heat required by both the preheating and the catalyzing tubes. After about thirty days' use it is necessary to stop the flow of gas through a set of catalyzers and blow air through them in order to burn off the deposited carbon which is found to be, at times, 50 per cent in excess of the quantity calculated from the amount of carbon bisulfide reduced to hydrogen sulfide. This carbon may be obtained from the decomposition of hydrocarbons in the gas, but analyses of the gas made before and after treatment, which are given below, show that the quantity so decomposed is negligible.

No information has been given as to the cost of operating this process and although it does not require the maintenance of as high a temperature as is employed in the Hall and Papst process it would seem to be somewhat more complicated and expensive even though no loss of nickel be suffered.

	Gas before treatment Per cent	Gas after treatment Per cent
CO <sub>2</sub> .....	1.82	1.80
C <sub>2</sub> H <sub>2</sub> .....	3.61	3.79
O <sub>2</sub> .....	0.27	0.07
CO.....	8.85	8.62
CH <sub>4</sub> .....	26.62	27.45
H <sub>2</sub> .....	52.45	52.19
N <sub>2</sub> (by difference).....	6.38	6.08
Illuminating power in English candles.....	100.00	100.00
Calorific value, B. t. u. per cu. ft.....	14.05	14.05
	590.00	594.00

#### SODA-CELLULOSE FOR REMOVAL OF CARBON BISULFIDE

Another process which has been tried only at an experimental plant of the Heidelberg, Germany, Gas Works consists in treating the gas, entirely freed from tar, ammonia, sulfureted hydrogen and carbon dioxide, with a compound of soda and cellulose obtained by treating cellulose sulfite with soda lye. The resulting material, after having been rolled and crumbled to a powder, is placed on trays in purifying vessels in the same way as oxide of iron. When brought into contact with carbon bisulfide the soda cellulose is changed into cellulose xanthogenate or viscose, the raw material from which are obtained cellulose hydrate and the formyl-cellulose used in the manufacture of non-inflammable celluloid. In the experimental plant ten tons of the soda cellulose material, known as "Athion," absorbed 1.25 tons of carbon bisulfide so that with gas containing 45 grains per 100 cu. ft., ten tons would purify over 35,000,000 cu. ft. of gas, but the cost of operation is not given.

Since it is not the custom in the United States to remove carbon dioxide from illuminating gas, the employment of this process would involve the installation of additional apparatus for that purpose.

#### OXIDE OF IRON CATALYZER FOR DECOMPOSITION OF CARBON BISULFIDE

A very promising process, which, however, has not yet been tried out on a working scale, is based upon the fact that at temperatures above 100° F. metallic iron acts as a catalyzer that brings about and accelerates the reaction between bisulfide of carbon and moisture in illuminating gas. The fact that gas, free from sulfureted hydrogen originally, contained this substance after having passed through a wrought iron service pipe which, because of running near a steam pipe, was heated to temperatures varying between 90° and 158° F., attracted the attention of Mr. J. G. Taplay and a number of experiments made by him showed that at a temperature of 158° F. the reaction between the bisulfide of carbon and moisture with the formation of sulfureted hydrogen took place quite rapidly, in gas traveling through a wrought iron pipe, and also that as the interior of the pipe became rusted the sulfureted hydrogen produced was absorbed by the oxide of iron and did not show at the outlet of the pipe.

A French gas engineer, M. Guillet, observed the same action taking place inside a gas holder and by experiments determined that when gas containing bisulfide of carbon was passed through ordinary oxide of iron purifying material at temperatures above 25° C. (72° F.) 25 per cent of the original content of carbon bisulfide was removed. He found 100° C. (212° F.) to be the temperature at which the change became interestingly rapid, while at a temperature of 130° C. (266° F.) more than 67 per cent of the bisulfide of carbon originally present was converted into hydrogen sulfide and removed as the gas passed through the material. The percentage removed increased with the amount originally present, the treated gas containing only from 3.01 to 5.82 grains, while the original gas contained from 9.48 to 24.42 grains of bisulfide of carbon per 100 cu. ft.

Since the efficiency of oxide of iron for the removal of sulfureted hydrogen is very much increased by heating and it should not be difficult to maintain the temperature of the purifying material at the comparatively low temperature of, say,



250° F. this process would seem to offer the simplest and most inexpensive means of removing from illuminating gas the larger portion of the bisulfide of carbon which it still contains after the treatment ordinarily given to it in gas works, whenever the amount of this impurity present is sufficiently large to make it important that it should be reduced.

84 WILLIAM STREET, NEW YORK

### CHEMISTRY AN IMPORTANT FACTOR IN THE FERTILIZER INDUSTRY<sup>1</sup>

By J. E. BRECKENRIDGE

Not so many years ago the fertilizer manufacturer looked upon the chemist as a non-producing something, which was a necessary evil. Friction continually existed between superintendent and chemist, the superintendent being sure that materials were batched on correct weights and that the chemist was wrong if the analyses did not come up to the guarantee. In one factory where a man inspected the cars of tankage as they were received and classed them by looks, as 8, 9 or 10 per cent goods, the superintendent said that this man could guess nearer than the chemist could test. Such conditions were not unusual in factory management. Rock, acid, potash salts and ammoniates were all combined wet, and it was not unusual to have to allow 10 per cent excess for potash, because it would not show as water-soluble in the final product. No account was taken of the actual chemical action when phosphate rock containing iron, alumina, silica and fluorine was mixed with sulfuric acid and potash salts added.

Conditions at the present time are entirely changed. Successful manufacturers insist that superintendent and chemist work together, and that all chemical action influencing the analysis of mixed fertilizers be carefully watched so that there shall be the greatest efficiency of the materials used. The superintendent should be held responsible for the pounds received of phosphoric acid, potash in terms of  $K_2O$ , and nitrogen, and unless conditions affecting the loss of available phosphoric acid, water-soluble potash and nitrogen are understood, the greatest efficiency will not be realized.

The manufacture of acid phosphate is one of the oldest processes now in use in the industry. Not long ago, we were satisfied with 16 per cent available phosphoric acid from 66 per cent calcium phosphate Florida rock. Now we are not satisfied unless we get 17 to 17.5 per cent available from the same grade of rock. Then it was unheard of to obtain 16 per cent available phosphoric acid from 62 to 63 per cent calcium phosphate Charleston rock; now this is possible. Such results are entirely due to taking advantage of every possible condition which affects chemical reaction, such as fineness of rock, strength of acid, time of mixing and manipulation of acid phosphate from dens to storage.

The possibilities of phosphoric acid compounds from phosphate rock and sulfuric acid have hardly been considered, due largely to the presence of arsenic. This condition no longer exists, as it is possible to reduce the arsenic content in phos-

phoric acid made from phosphate rock and sulfuric acid to a percentage that will pass the pure food standard. Hence, chemistry aids the fertilizer industry by producing the phosphoric acid not only for the soil, but for general phosphoric acid compounds. Again, electrochemistry offers, to the fertilizer industry, possibilities of securing very high temperatures and thus rendering available the phosphoric acid in refractory minerals. Fluorine compounds are now being made from the flue gases from acid phosphate manufacture, which has been made possible only by taking advantage of chemical reaction.

Chemistry has made rapid strides for the benefit of the industry from the nitrogen standpoint. We no longer have to rely on animal, mineral and vegetable ammoniates, since nitrogen recovered from the air helps to increase the supply and thus regulate prices. Chemistry has increased the nitrogen supply available for soil by giving us the conditions necessary for rendering inert nitrogen available, thus allowing us to use many waste materials.

Nature has accomplished most for the industry in regard to potash, for the natural deposits seem to outclass anything that has been done in giving us supply of this element. Possibilities of feldspar and alunite potash are still in the distance, as well as the recovery of beet sugar molasses potash by passing the molasses over zeolites, when the potash is said to be held so that it can be recovered from the zeolite.

Chemistry again gives promise of potash from kelp, where the actual cost of the potash may be reduced by the income from by-products. Cement furnaces also are being investigated, where it may be possible to volatilize and recover the potash contained in the raw materials.

Chemistry has an important place in the fertilizer industry in relation to the conditions which affect drilling of fertilizers. If the materials at hand were always the same as to chemical composition, little trouble would be experienced in mixing them. But there are so many varying materials, and so many varying compositions, that unless foresight is used as to the chemical reactions possible where materials are mixed, serious trouble will result.

Chemistry again aids the fertilizer industry in chemical engineering problems that are common to power plants.

Chemistry is the basis of all commercial values in the fertilizer industry. Where we consider that profits may be easily turned to losses by incorrect chemical work, it must be realized that the fertilizer manufacturers must have able and competent chemists to do their work.

There is much work ahead in the fertilizer industry. Unless every effort is used to develop reliable methods for chemical analysis, and research work is carried on to increase the supply of fertilizer materials, and unless chemical conditions affecting fertilizer manufacture are carefully studied to the end that greatest efficiency be gained, the chemist will not have done his part in the development of this industry.

CARTERET, NEW JERSEY

## OBITUARIES

### HERMAN FRASCH

With deep regret we record the death of Mr. Herman Frasch, the distinguished chemical engineer, which occurred in Paris, on May 1, 1914.

Mr. Frasch was born in Gaildorf, in Wurtemberg, in 1852, and received his early education as an apothecary in Germany. In 1868, he came to America and was, for a time, in charge of the laboratory of Professor Maisch of the Philadelphia College of Pharmacy. Being particularly interested in Industrial Chem-

istry, he established a laboratory in Philadelphia, in 1874, in which he began a series of investigations which led to some of the most brilliant achievements in the field of chemical engineering.

His first invention was a process for refining paraffin wax in 1876. This process was a great success and was followed by his invention of a process for the refining of the sulfur oils of the Canadian, Ohio, and Illinois fields. Previous to this invention, these inferior oils had a very low market value and were limited to use as fuel oils. In 1885, he organized the Empire Oil Company and established a small refinery at London, On-

<sup>1</sup> Chairman's address, Fertilizer Chemistry Division, 49th Meeting A. C. S., Cincinnati, April 6-10, 1914.

tario, for the purpose of developing his desulfurizing process on the Canadian oils. As a result of this work, the methods of refining sulfur oils were revolutionized, and plants for working these oils were established at Cleveland, Whiting and other centers.

Another wonderful invention was his process for extracting sulfur from the great Louisiana deposit. That this deposit existed, covered by a layer of quicksand over five hundred feet thick, had been known since 1865. Company after company was organized to develop these sulfur mines but without success until Mr. Frasch purchased the property in 1891, and attacked the problem from an entirely new standpoint. Instead of attempting to sink a shaft and mine after the customary practice, he drove wells through the sand and inserted a series of iron tubes so arranged that he was able to fuse the sulfur in place by forcing down superheated water under high pressure. The molten sulfur was permitted to flow to the surface through return pipes where it was run into large bins and solidified in commercial form. This enterprise has been in successful operation ever since and supplies all the sulfur required for the United States market with some excess for exportation.

I do not, on this occasion, go into details with regard to the other remarkable inventions of Mr. Frasch, for the reason that in December, 1911, the associated chemical societies of America conferred upon him the Perkin Gold Medal which is awarded annually for distinguished service in the field of applied chemistry, and the proceedings on that occasion were printed in full in THIS JOURNAL, in the issue of February, 1912, page 131, and included the address of acceptance by Mr. Frasch, in

which he gives some details of his most interesting career.

Mr. Frasch was a member of The American Chemical Society, The Society of Chemical Industry, The American Institute of Chemical Engineers, The American Institute of Mining Engineers, The American Electrochemical Society, The Verein Deutscher Chemiker, and The Chemists' Club, New York City.

C. F. CHANDLER

#### RESOLUTIONS PASSED BY CHEMICAL SOCIETIES

At a meeting of the officers of the undersigned chemical organizations, held on the 17th day of May, 1914, the following resolutions were adopted:

The members of the chemical profession as represented by the officers of the chemical and allied societies, have received, with profound sorrow, the sad tidings of the demise of their distinguished colleague and fellow member, Mr. Herman Frasch.

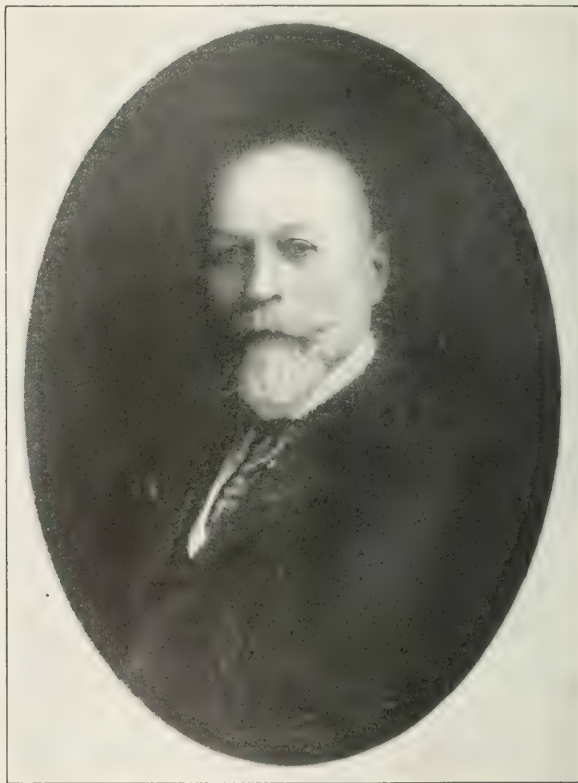
His life, his energies and his wide knowledge were given freely and unselfishly to the development of the chemical industry. As a creator of new branches of applied chemistry his name is among the most illustrious, and in the history of technical accomplishment his work stands out as an inspiration to all coming generations.

Much as we honor his memory as a chemist, he has no less endeared himself to us as a man, as a wise counsellor and as a friend.

Notwithstanding the stress of an extraordinarily active life, he preserved within his heart a great kindness and consideration towards others and an ever ready sympathy in their efforts and struggles.

Resolved, that these resolutions be spread upon the minutes of the undersigned societies and that they be engrossed and copies presented to his widow and his daughter, to whom we extend our deepest sympathy in their bereavement.

THE CHEMISTS' CLUB  
NEW YORK SECTION  
AMERICAN CHEMICAL SOCIETY  
NEW YORK SECTION  
SOCIETY OF CHEMICAL INDUSTRY  
AMERICAN INSTITUTE OF  
CHEMICAL ENGINEERS  
NEW YORK SECTION  
VEREIN DEUTSCHER CHEMIKER  
NEW YORK SECTION  
AMERICAN ELECTROCHEMICAL SOCIETY  
PERKIN MEDAL COMMITTEE



HERMAN FRASCH

#### PAUL L. V. HÉROULT

Paul L. V. Héroult, the inventor, died at his home in Paris, on May 13th. He was born April 10, 1863, at Thury-Harcourt,

Calvados, France, the son of Patrice and Elise Lepetit-Desaunay Héroult. His father was a tanner in Paris and his grandfather a leather broker in London. Both branches of the family had come originally from Normandy. As a boy he was educated in London, afterwards entering the Lycée de Carn, Calvados, France. His education was completed at the College Sainte Barbe and the École des Mines in Paris.

Mr. Héroult invented and patented, in Europe, in 1886, a process for the manufacture of aluminum. The United States Patent Office records disclosed the fact that the same process had been invented in America at about the same time, by Charles

M. Hall. As a result of the controversy, the European patents were granted to Hérault and the American patents to Hall.

In 1887, Mr. Hérault became the technical manager of the aluminum works at Neubrausen, Switzerland, and in 1890, was made director of the French Aluminum Company.

He spent much of his time in chemical engineering research, and in 1899, developed an electric furnace for the production of steel. He was connected, in the development of this electric steel

furnace, with The United States Steel Corporation, The Crucible Steel Company of America, Halcomb Steel Company, Electro-Metals Company, the Aktiebolaget Héraults, Elektriska Stal, Sweden, and Edgar Allen, Thomas Firth and Vickers, all of Sheffield, England.

Mr. Hérault was a member of The Chemists' Club, New York, The American Electrochemical Society, The American Society of Mining Engineers, The Société des Ingénieurs, Paris and The Faraday Society, London.

## CURRENT INDUSTRIAL NEWS

By M. L. HAMLIN

### A NEW TYPE OF ARTIFICIAL FERTILIZER

In a paper read before the Society of Arts of London by Professor W. B. Bottomly, a new type of fertilizer was described, which, according to *Engineering* (London), 97 (1914), 359, threatens serious competition with the products of the electric furnace. After giving an account of various previous attempts to utilize for fertilizing purposes the power of certain bacteria found on the roots of some plants to fix atmospheric nitrogen, and showing how these attempts had been unsuccessful, Professor Bottomly described experimental work carried on at the botanical laboratory of King's College, claiming that it had been attended with complete success. It was found that suitably treated peat formed a most excellent medium for the growth of the bacterium, and soils manured with this peat have shown a marked enhancement of their fertility. Before inoculating the peat with the bacterium in question the raw peat has to undergo a preliminary treatment by another bacterium, which was found to have the power of converting natural peat into a humated neutral medium. Attempts to achieve the same end by neutralizing the humic acid of the peat by alkalies resulted in complete failure. The peat after inoculation with the special bacterium is kept at constant temperature for a week or ten days, after which period it is sterilized by the action of live steam. It is then inoculated afresh with a mixture of *azotobacter chroococcum* and *bacillus radiicola*, and after a few days' incubation at 26° C., is ready for use. The following table shows the effect of the treatment as proved by analysis. Analyses of a garden soil and other manures are also given for comparison:

	Soluble humate Per cent	Soluble nitrogen Per cent	Total nitrogen Per cent
Raw peat.....	0.028	0.214	1.267
Bacterized peat.....	15.194	2.694	4.310
Garden soil.....	0.012	0.026	0.427
Fresh soluble manure.....	0.433	0.291	2.533
Well-rotted stable manure.....	1.46	0.439	2.848
One-year-old peat-moss litter manure.....	1.05	0.826	2.587

An important point is that the azotobacter continue to flourish after the peat has been added as manure to the soil to be fertilized, thus fixing further nitrogen. In a series of comparative experiments made on an exhausted soil the new manure showed the following percentage of advantage over its competitors:

CROP	Inoculated peat Per cent	Artificials Per cent	Farm dung Per cent
Potatoes.....	123	75	41
Turnips.....	100	47	26
Beet.....	281	54	43
Onions.....	110	110	46
Carrots.....	260	20	28

With fertile soils the addition of a very little of the treated peat is stated to give a very large increase in the rate of growth. This is believed to be due to the presence in the peat of accessory food bodies, for which a special search is now being made.

### A NEW COAL CALORIMETER

An interesting new coal calorimeter is that recently introduced by Macklow-Smith and described in *Engineering* (London), 97 (1914), 385.

The calorimeter consists essentially of an outer jar of glass provided with a reference line indicating the height to which it is to be filled with water in making an experiment. From the edges of this jar a crucible support is slung by the spring clips shown in Fig. 1. A piece of lampwick, impregnated with sodium or potassium nitrate, is embedded in a briquette of the coal under test, and is ignited by a match as indicated.

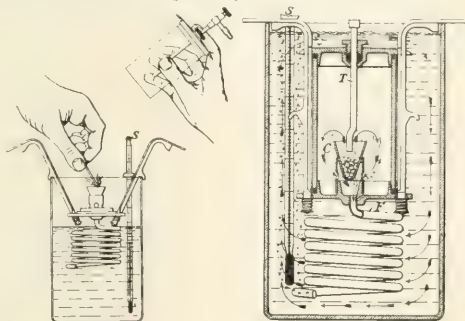


FIG 1

FIG 2

The glass bell, shown to the right in Fig. 1, is next lowered over the crucible and clamped, against a rubber ring, by springing back the supporting clips into their working position, as indicated in Fig. 2. A supply of oxygen is led from the oxygen bottle through an automatic reducing-valve and the flexible pipe to the inlet pipe T, which, as will be seen, is fitted with an additional regulating valve, D. This oxygen causes the coal to ignite, and the products of combustion flow through the coil F, and escape through small holes near the end of it, and finally pass up through the water. In their journey these gases part with their heat, and at the same time thoroughly stir the water up. A series of readings of the thermometer S are taken at equal intervals of time, and plotted against a time base, for determining the radiation correction. Simultaneous observations are, of course, made of the room temperature. The maximum temperature recorded on the plot is noted, and the temperature rise deduced from this is corrected, for the loss of heat externally, by means of a table of coefficients supplied with the instrument. The water equivalent of the coil and bell and other components of the calorimeter is also supplied by the makers, and as a consequence the user has merely to fill the apparatus to the level engraved, and may then treat the whole as having a constant specific heat, and obtain his results by multiplying a constant (provided by the makers) by the corrected temperature rise, and then dividing this product by the weight, in grams, of the coal taken.



While the briquette form is the most convenient in which to burn the coal, powdered coal may be and often is used. In actual operation the circulation of the water in the calorimeter is very perfect and regular at all rates of combustion, so that not only is the whole of the apparatus raised to the same temperature with certainty, but the radiation is also very regular in character. The amount of radiation while the water is being circulated is very different from that under quiescent conditions.

### ELECTRIC SMELTING OF IRON AT HARDANGER, NORWAY

The hitherto unsatisfactory results of electric smelting at Hardanger were discussed at a recent meeting of the Polyteknisk Forening of Kristiania by Gustaf Ödquist, *Chemiker-Zeitung*, 38 (1914), 294. The reason for the failure lies in a series of unfortunate coincident circumstances, and not, according to Ödquist, in the type of furnace used. These furnaces are, however, not adapted to the use of coke for reduction, the electrodes being probably too large in diameter, and an economic use of power is rendered impossible by the large variations in load which make it necessary to have at command more than 800 k.w. in excess of the average amount of electricity used. The experience of the Hardanger works has shown that iron smelting with coke is possible, but not economical with the system used at present. Although charcoal is considerably more expensive than coke, the Hardanger iron cost \$3 to \$4 more per metric ton than Swedish iron reduced with charcoal.

In the discussion, the opinion was expressed as the result of recent experiments that by a slight change in the construction of the furnaces iron could be produced even from low-grade ores, using coke as the reducing agent, that could compete with the Swedish iron.

### THE FLUXOGRAPH FLOW RECORDER

A measuring instrument that promises to be of value through a wide range of applications is the "Fluxograph" flow recorder, recently put on the market and described in *Engineering* (London), 97 (1914), 284. It is an appliance for the accurate measurement and registration of the flow of water or any liquid by means of the V-shaped notch discharge method, based on the formula

$$Q = cH^{3/2}$$

proposed by Mr. James Thomson, M.A., D.Sc., LL.D., F.R.S., Professor of Civil Engineering at Queen's College, Belfast, and at Glasgow University. The results of his investigations are given in the subjoined table, where:

H = the vertical height in inches of the still water level from the vertex of the notch.

Q = the corresponding discharge over the notch in cubic feet per minute, as found by experiment.

c = the value of the coefficient calculated from the formula  $Q = cH^{3/2}$ .

H	Q	c
7	39.69	0.3061
6	26.87	0.3048
5	17.07	0.3053
4	9.819	0.3068
3	4.780	0.3067
2	1.748	0.3088

The figures contained in the above table give the average results for the series of experiments made in the years 1860 and 1861. The mean of the six values of c is 0.3064, but from a comparison of his experiments Professor Thomson finally adopted 0.305 as the coefficient, and gives as his formula for the right-angle notch:

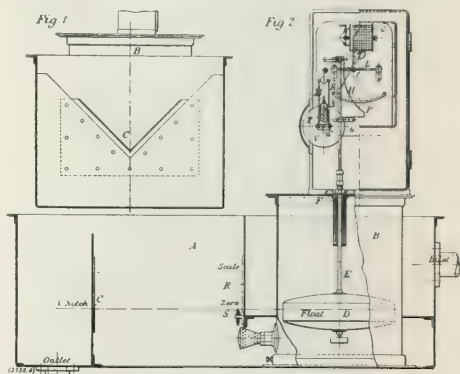
$$Q = 0.305 H^{3/2}$$

The total results of later observations proved how remarkably

accurate Dr. Thomson was when he gave 0.305 for the average value of the coefficient c for heads ranging from 2 in. to 7 in.

In the Fluxograph recorder is presented a practical and commercial application of the results of this valuable research work. Devised with the object of meeting the demand for a reliable integrating or weir meter, a number of these instruments have already been installed and successfully employed in various capacities. The machine, in addition to registering permanently upon a ruled chart the rate of flow at any moment in gallons per hour, also provides, by means of a pointer on a figured open-scale dial, a simple method of reading off directly, without calculation, the amount of water passing at any instant. Figs. 1 and 2 will serve to illustrate the machine and make its action clear.

On referring to the engravings, it will be seen that after entering the right-hand compartment of the measuring-tank A, Fig. 2, the water passes through baffling and diaphragm plates, and becomes tranquil before passing over the V-notch C, shown in Fig. 1, which is a transverse section through Fig. 2. A large float, D, is situated in a cylinder, B, to which the water gains access through a grid, and in which the level is the same as in compartment A. According to the variation of the water-level, so the float rises or falls, and it is this movement of rise and fall that actuates the mechanism of the recorder. At the point where the float-rod passes through the bottom of the instrument-



case a vapor-seal and dust-excluder arrangement, F, is fixed to prevent the working parts from getting clogged or becoming affected by rust. Sliding through a frictionless roller-bearing, G, the float-rod carries a flat compensating-curve attachment, H. The pen-carriage J, on which the pointer K is also fixed, moves along silver-steel bearing bars L, and is kept in roller contact with the face of the compensating-curve H by means of a counterweight, M (see Fig. 2).

It will be seen that the rise and fall of the water causes the float D to make a corresponding movement, and the float accordingly operates the compensating curve H, which ensures that the movement of the pen O and the pointer K is directly proportional to the amount of water flowing over the weir. While the pointer K momentarily indicates upon an open-scale figured dial, P, the rate of flow in gallons per hour, the pen O makes a permanent record of that quantity upon a chart, Q, surrounding the rotating drum of a clock device. With the aid of a planimeter the total amount passed can be obtained from the area of the chart record. The actual depth of water passing over the weir can be observed at any moment, and the accuracy of the recorder can be independently checked by means of a vertical scale, R, marked in inches, which is fixed on the measuring-tank A, in correct relation to the zero pointer S and bottom of the V-notch C, as shown in Fig. 2. Oftentimes it is imperative to be able to

read off directly and quickly the total quantity of water that has flowed for a given period. A simple form of friction integrator, T, is described herewith.

A clock, not shown, affixed to the recorder case, drives a flat aluminium disc, V. Kept in light contact against the disc is a small fiber wheel, W, connected to the counter or integrator. The latter is attached to the pen-carriage J, which is actuated by the movement of the float-rod compensating curve H according to the rise and fall of the float, so the driving-wheel W and the counter X moves away from or towards the center of the disc V.

When no water is passing over the V-notch C, the counter-wheel W remains stationary at the center of the disc, where, of course, no motion is transmitted. When the water is flowing through the notch, the float D rises, and, through the compensating curve P, raises the apparatus and lowers the counter proportionately, not to the rise of the float, but to the volume flowing through, so that the integrator is driven at a speed proportional to the amount passing over the weir. Figures showing the total quantity of flow can be read off directly from the counter-dials Y. The fact that the driving of the counter is continuous and positive ensures that all liquid must be registered.

The Fluxograph flow-recorder is well suited for the measuring and recording of water supplies, boiler-feed, air-pump discharge, sewage or trade effluents, compensating water from reservoirs, and for oils, acids, and alkalies used in manufacturing processes.

### INDUSTRIAL ACCIDENTS IN MASSACHUSETTS

The Industrial Accident Board of Massachusetts, at the end of its first year reports the total number of non-fatal accidents in the state as 89,694, or about one for every ten wage earners. The board believes that at least half of these can be prevented by improved inspection methods, by safeguarding machines before they leave the factory, by the maintenance of safety museums, through lectures, moving pictures, school talks and the elimination of danger spots in plants. There were 474 fatal accidents, classified as follows:

Railroad equipment.....	119	Belting.....	6
Falls.....	66	Infection from trivial cuts, burns, etc.....	5
Vehicles.....	43	Saws.....	4
Hand labor.....	37	Explosions (not boiler).....	4
Elevators.....	33	Hoists.....	4
Electricity.....	25	Illness.....	3
Street railways.....	20	Presses.....	2
Boiler explosions and burns.....	15	Gears.....	2
Excavating.....	14	Emery wheels.....	2
Cranes.....	11	Occupational diseases.....	1
Miscellaneous.....	11	Glass.....	1
Asphyxiation, drowning, etc.....	10	Wood molders.....	1
Animals, insects, etc.....	9	Assault and fighting.....	1
Shafting, set screws, etc.....	9		
Falling material.....	8	TOTAL.....	474
Machinery peculiar to special industries.....	7		

### VACUUM TAR

*Scientific American*, Apr. 25, 1914, reports that by distilling coal under a vacuum of 15 mm. of mercury, Pictet and Bouvier obtain a so-called "vacuum tar," this appearing to be quite different from usual coal tar. Such tar contains no phenol or aromatic carbides, and when oxidized by permanganate, the products are acids of the fatty series. The properties of this tar resemble those of Caucasus petroleum which consists of hydro-aromatic carbides. These experiments tend to confirm the hypotheses advanced by Berthelot and others as to the formation of the constituents of tar.

### REQUIREMENTS OF GLASS FOR BOTTLING MEDICINE

W. A. Hamor in the *American Druggist and Pharmaceutical Record*, 62 (1914), 29, states that owing to the want of or negligence in chemical control at the factories, the glasses from which bottles are made often present wide divergences in composition, the principal variations being in content of silica, calcium oxide

and magnesium oxide.<sup>1</sup> The limestone in use by many manufacturers varies considerably in magnesium oxide and carbon dioxide content, and it has been ascertained<sup>2</sup> that variations of calcium oxide in the "batch" cause lack of homogeneity. It follows, therefore, from these facts alone, that not only should the materials entering into the batch mixture comply with standard specifications and accordingly be under analytical control, but also the composition of the "batch" itself should be based entirely thereon.

A large number of cases of deterioration of chemical products, due to the alleged solubility of bottle glass, have been noted by various consumers. In the case of non-actinic glass bottles, such alteration in composition may often be ascribed to the fact that the glass yields sufficient alkali to cause contamination or decomposition; but in the case of colorless glass bottles the cause of any deterioration is more dubitable, providing the product contained therein is subject to photolytic action. Certain it is, however, that medicinal preparations, like reagents, should be kept only in bottles made of high-grade glass, and that more consideration should be given to the fact that not only is amber glass non-actinic, thereby screening out light rays occasioning decomposition, but it is also usually much less soluble than colorless glass.

A number of preparations affected by light (for instance, compound glycerophosphates) are supplied by some manufacturers in colorless glass bottles; whereas others (for example, codliver oil) affected by even slight amounts of alkaline matter from glass, occasionally present indications that the glass bottles in which they are supplied are soluble.

A question of importance in the trade is: With what conditions should the glass of medicine bottles comply? Lenz<sup>3</sup> has proposed that if the bottle is half filled with distilled water and then heated in boiling water for six hours, with frequent shaking, the amount of alkaline matter extracted should not exceed 1.5, or, at the most, 2.5 mg. per sq. dm.; while Moeller<sup>4</sup> considers that medicine bottles should not yield any alkali to water heated in them for three hours.

Glass sufficiently pure for medicine bottles should not, in the writer's opinion, lose more than six mg. of alkali per square dm. and should not show pronounced cracks when kept for twenty-four hours in boiling distilled water. It is sufficient to specify, however, that all bottles intended for medicinal purposes should show no alkaline reaction when filled with distilled water containing several drops of phenolphthalein solution and heated at 100° C. for six hours. This requirement is simple, yet experience has demonstrated its efficacy in practice.

In this connection reference may be made to the shape of bottles intended as containers for poisons. It has been proposed that these should be hexagonal. A most striking form is triangular. A bottle of this shape, made of dark red glass, would fill an obvious need.

### METHOD OF SCURFING GAS RETORTS

The *Journal of Gas Lighting and Water Supply*, 125 (1914), 295, describes a method of scurfing retorts presented in a communication by M. Schmidt to the Belgian Gas Association. The appliance used is a "Centrator" blower, actuated by a 2 H. P. gas-engine. It makes from 3600 to 3900 revolutions per minute, and in this period delivers 700 cubic feet of air at a pressure of about 6 inches of water. The blower is worked by means of encased steel rollers, which have to be kept well lubricated; these rollers are replaceable. The engine and blower combined occupy but little space. The carriage measures only 4 ft. by 3 ft., and it can be easily moved. The engine cylinder is cooled by water conveyed by a flexible tube. When a retort

<sup>1</sup> For a general discussion of the Glass Bottle Industry in the United States, see Hamor, *THIS JOURNAL*, 6 (1913), 951.

<sup>2</sup> See *Trans. Am. Ceram. Soc.*, 15, 706.

<sup>3</sup> *Pharm. J.*, 91, p. 531.

<sup>4</sup> *Ibid.*

has to be scurfed, the machine is drawn up near the setting, and a pipe of galvanized or, ordinary iron is fixed from the outlet of the blower and run into the retort to about half its length. The engine is then started, and the removal of the scurf at once begins. About two hours only are required to clear a retort.

Taking the case of gas-works having ten settings of nine 10-feet retorts, M. Schmidt gave the total annual cost of scurfing reckoning twelve operations in a year, as \$266. Notwithstanding that the greater part of the graphite is burnt, an appreciable quantity is saved, the disposal of which helps to cover the cost of maintenance and the sinking-fund charges. Compared with similar works in which the old method is used, M. Schmidt gave the total annual expense for dealing with ten settings as \$608. From this there would have to be deducted the return from the sale of the graphite. From 10,000 to 12,000 kilos of this would be produced, worth \$120, which would bring down the cost to \$488. The other method, therefore, shows a saving of about \$222. The great advantage of forced injection of air is that the works are able to produce more gas, owing to the fact that the retorts can be charged more rapidly, thereby ensuring economy of labor and heating. Indeed, the productive capacity of the works is increased by about 3.5 per cent.

### INDUSTRIAL CONDITIONS IN FRANCE

*Engineering* (London), 97 (1914), 486, quotes the *Moniteur Industriel* to the effect that metallurgical and engineering works in the North of France, taken generally, did less business in 1913 than in 1912. In regard to mechanical industry, attention is called to the most active competition experienced on the part of Germany, Belgium, and the United States, which countries, notwithstanding high customs duties, succeed in selling their material at lower prices than the French products. Attention is also called to the insufficiency of the customs duty on certain classes of French manufactured articles, in the price of which the cost of labor forms the heaviest constituent. Complaints are raised in the article by the *Moniteur* concerning the orders placed abroad by the French railway companies; no organization, it says, which owns any concession in France should be allowed to give orders to neighboring countries unless it be ascertained beforehand as an absolute fact that French works cannot deliver them in the time stipulated. Loans made by foreign countries in France should carry with them stipulations to the effect that the material and machinery required by the said foreign countries should be ordered from French works.

### ELECTRIC TESTING BUREAUS IN GERMANY

Besides the Physikalisch-Technische Reichsanstalt in Charlottenburg which undertakes investigations and tests of the most various kinds, there are seven testing stations which are officially recognized as independent and impartial public laboratories for electrotechnological investigations (*Zeitschr. d. Ver. deutsch. Ing.*, 58 (1914), 559). These stations, at Ilmenau, Hamburg, Munich, Nuremberg, Chemnitz, Frankfurt-on-Main, and Bremen, have been organized as a corporation with a main office at the laboratory in Nuremberg.

### STEAM RAISING BY GAS COKE

The *Journal of Gas Lighting and Water Supply* has recently been devoting a good deal of space to the question of the advantages of gas coke for steam raising. E. W. L. Nicol discussing this subject in 125 (1914), 567, gives some comparative data, and reviews the present situation.

Raw bituminous coal is being used almost exclusively in England for steam raising, notwithstanding the enormous cost and inefficiency of distillation in an ordinary boiler furnace, and comparatively few engineers in charge of boiler plants have any first-hand knowledge or experience of coke fuel

for steam raising. An average of many analyses of ordinary bituminous steam coal (said to have been washed) shows the following:

Moisture Per cent	Fixed carbon Per cent	Volatile matter Per cent	Ash Per cent	Calorific value (dry) B. t. u. per lb.
10	45.6	32	12.4	12,500

When consumed in a boiler furnace for steam-raising, if any degree of efficiency is to be attained, the coal must be heated until the volatile gases are distilled off. This process absorbs about 10 per cent of the total heat in the coal. The distilled gases must then be liberally diluted with air, to burn them without excessive smoke production. This excess air must, of course, be heated to the furnace temperature, and is mostly rejected to the chimney as waste heat. As the diluted gas is ignited, it should be allowed to burn in a large brick-lined combustion chamber before coming in contact with the comparatively cool heating surfaces of the boiler, and the supply of air should be gradually diminished as the distillation process is completed. Meanwhile the solid residue or coke (which is smokeless, and requires about half the amount of air necessary for the complete combustion of the gas, to burn it under the best conditions) remaining on the fire-bars must be consumed in the same furnace at the same time. So it is evident when too much or too little air is being admitted to the furnace, whether the stoking be intermittent or continuous.

Gas coke is practically a simple mixture of carbon and ash, with little or no smoke-producing volatile matter. Uniform in quality and composition within fairly narrow limits, it requires no expert attention to obtain the most economical results during combustion, and the air supply to the furnace may be predetermined and fixed at the maximum desirable—the only adjustment left to the varying skill of the stoker being the fire thickness or density—one which cannot easily be neglected or abused.

Eminent authorities on the subject are agreed that the higher the volatile contents of a fuel, the more it is liable to smoke. The percentage of volatile matter in steam-raising fuel is in reality a measure of the difficulty of burning it under boilers with perfect combustion. Conversely, the lower the percentage of volatile matter, the greater the simplicity and efficiency of combustion. Low-volatile natural fuels are high-priced. They are known as anthracites and semi-anthracites; but the volatile contents of any solid fuel, as fired, may be adjusted to the most advantageous proportions by adding carbon in the form of coke.

The volatile contents of the coal detailed above might, with advantage, be adjusted by mixing with equal parts of coke as follows:

	Carbon Per cent	Volatiles Per cent	Calorific value B. t. u. per lb.
Coal.....	45.6	32.0	12,500
Coke.....	88.0	2.5	13,000
Mixture.....	133.6	34.5	25,500
	66.8	17.2	12,750

### Typical South Wales anthracite analyses:

Carbon Per cent	Volatiles Per cent	Approximate B. t. u. per 1 d. (\$0.02) of cost, at, say, 25 s. (\$4.25) per ton
93	3	108,750

### Good quality gas coke analyses:

Carbon Per cent	Volatiles Per cent	Approximate B. t. u. per 1 d. (\$0.02) of cost, at, say, 19 s. (\$4.25) per ton
88	2.5	130,000

In using so-called smokeless coal at comparatively high prices when gas coke is available at reasonable cost, steam users may not, therefore, be operating their plant to the best advantage.

All bituminous fuels, when fired under boilers, require very careful management, and large brick-lined combustion chambers must be provided if they are to be consumed without excessive



smoke or loss due to the escape of unburnt hydrocarbon gases.

Gas coke is smokeless, contains no hydrocarbons, and does not require any combustion chamber. It may, with advantage, be consumed in contact with the boiler-tubes and heating surfaces. Where gas coke is used, the combustion process is much easier to control, and the risk of loss in the form of unburned carbon (black smoke) and hydrocarbon gas is avoided.

All bituminous coals contain sulfur. On heating a boiler-furnace, the volatile sulfur is liberated and burnt to form  $\text{SO}_2$ , which may cause serious damage by attacking the metal and furnace brickwork. In coke-fired water-tube boilers, tube failures, due to this cause, are comparatively infrequent, for the carbonizing process necessary to produce coke eliminates, to a great extent, this objectionable element.

Besides these data of Mr. Nicol, the journal presents (same volume, p. 363) the following figures, published by S. Tagg in the *Bulletin of the British Commercial Gas Association*:

POUNDS OF WATER EVAPORATED AT 100 LBS. PRESSURE PER POUND OF FUEL

Coke screenings through $\frac{3}{4}$ -inch diameter perforations	5.0
Large screened coke	6.7
Best Arley rough slack	7.5

### A MERCURY ENGINE

A paper read before the American Institute of Electrical Engineers by Mr. W. L. R. Emmet is reported in *Engineering* (London), 97 (1914), 498. In it is described some highly interesting experimental work undertaken to ascertain the feasibility of employing mercury as the working agent of a heat-engine. Mercury boils at  $677^\circ \text{F}$ . at atmospheric temperature, and condenses under a 28-in. vacuum at  $455^\circ \text{F}$ . The proposal is to use the mercury vapor in a turbine, using the exhaust to generate steam in a contrivance which is at once a condenser for the mercury and a boiler for the steam; the steam thus produced is to be utilized in a steam turbine. The physical properties of mercury render it, in some regards, very well adapted for use as the working agent in a turbine. Its high temperature is associated with a very moderate pressure. It is perfectly clean in use, so that its boiler will never require cleaning, and it appears from Mr. Emmet's experiments that, as it does not wet the blades through which it passes in the turbine, it has no tendency to erode them. Its high density makes possible a very moderate blade speed and a simple design of turbine. Some data as to the physical constants of mercury are quoted by Mr. Emmet as follow:

Specific heat of liquid mercury	= 0.0373
Specific heat of gaseous mercury	= 0.0248
Latent heat at 25 lbs. absolute	= 117 B. t. u.
Latent heat at 15 lbs. absolute	= 118 B. t. u.
Latent heat at 28 in. vacuum	= 121 B. t. u.
Latent heat at 29 in. vacuum	= 121.5 B. t. u.

The disadvantages of the mercury are its cost, which is about \$0.67 a pound, and its poisonous character if it escapes. There are, moreover, Mr. Emmet states, certain difficulties in confining both the vapor and the liquid, but these are not serious. As for the question of cost, the experiments made have led Mr. Emmet to think that not more than \$10 worth of mercury would be needed per kilowatt of output, and this is a higher and not a lower limit. A tandem mercury-steam plant would, he claims, show, a gain of 44 per cent on the output per pound of fuel burnt. A boiler of considerable size is now under construction in order to investigate the matter further.

### A EUROPEAN VIEW OF THE MONROE DOCTRINE

The part played by the United States in the industrial situation in South America is the subject of an article by L. W. Schmidt in *Technik und Wirtschaft*, 7 (1914), 174. The author shows how the Monroe doctrine, as originally applied to the question of territorial holdings, although surrounded by a nebula of uncertainty and never officially recognized by European na-

tions, was nevertheless a powerful influence in international relations. Now it seems to be the intention of the United States to apply the doctrine to the field of commerce and industry, an intention proved, says the author, by Lord Murray's recent failure to obtain concessions in Ecuador, Colombia and Costa Rica. This application of the doctrine was backed by popular opinion which had been worked up to a fever heat by the canal tolls question and so was in a condition to swallow whole the rumor of a second isthmian canal projected by the Pearson interests which was so diligently exploited by the yellow press.

Naturally, the expansion of the Monroe Doctrine in this direction aroused the mistrust of Europe, particularly since Europe, being the largest investor in South American development, has had the biggest share in her trade. While, however, the exports of the United States were comparatively small at the end of the last century, they have since then increased enormously; exports to Central America and the West Indies have risen from \$100,000,000 to \$180,000,000 and those to South America from \$38,000,000 to \$132,000,000. The following table gives data for the years 1902, 1906, 1909 and 1912:

UNITED STATES EXPORTS TO CENTRAL AND SOUTH AMERICA

	1902	1906	1909	1912
British Honduras	\$ 8,125,000	\$ 1,160,000	\$ 1,135,000	\$ 1,542,500
Costa Rica	14,762,500	2,455,000	2,422,500	3,830,000
Guatemala	17,650,000	3,072,500	1,792,500	2,645,000
Honduras	10,332,500	1,712,500	1,575,000	2,385,000
Nicaragua	14,267,500	1,967,500	1,422,500	2,612,500
Panama		13,082,500	17,637,500	24,725,000
Salvador	9,375,000	1,470,000	1,535,000	2,542,500
Mexico	41,867,500	61,090,000	52,282,500	55,490,000
Cuba	27,935,000	50,152,500	46,107,500	65,312,500
Argentine Republic	10,292,500	34,307,500	35,397,500	55,815,000
Bolivia	92,500	155,000	887,500	1,040,000
Brazil	10,910,000	15,257,500	18,405,000	36,412,500
Chile	3,900,000	9,100,000	5,765,000	16,267,500
Colombia	10,447,500	3,665,000	3,862,500	6,037,500
Ecuador	1,535,000	2,110,000	1,942,500	2,250,000
Paraguay	177,500	55,000	55,000	170,000
Peru	2,687,500	5,075,000	4,785,000	5,797,500
Uruguay	1,665,000	3,052,500	3,527,500	7,225,000
Venezuela	2,932,500	3,420,000	2,695,000	4,940,000

The reason for this increase is largely the fact that the development of commercial influence has gone hand in hand with the strengthening of intellectual influence. Where the rich young South American formerly went to Paris to round out his education, he now goes to New York or some other North American metropolis, and this indirect introduction of American ideas and ideals has found a more or less fertile soil in the unstable social and political conditions largely due to the mixed character of the population—whites, mestizos and Indians. While Europe, by investing large sums to develop natural resources, is expending her energy in preparing a sound economic foundation for the new race that will develop in South America, North America has followed other and more idealistic aims which may have a more lasting effect than the work of Europe.

Though the Monroe Doctrine has never seriously been put to the test, it has, nevertheless, had a real existence all this time, and has prevented any extended exercise of European influence in the southern continent. The United States has gone a step further, for in founding the Panamerican Union she has prepared a common ground for the interaction of common ideas and ideals which may, in time, aid in the formation of a possible confederacy, and at present aids in counteracting the great growth of European commercial influence. The evolution of this hundred-year old policy explains why the United States has left no stone unturned to prevent an influential European firm from obtaining land rights in Central America, where the possibility of a second interoceanic canal existed.

The history of South American commerce shows that those countries which have been in a position to invest the largest sums in commercial development have hitherto exercised the greatest influence, but that the United States is seeking her goal by other, perhaps more enduring, means and that she is looking ahead into a more distant future. But it is certain she cannot maintain her present rate of progress unless she is willing

to play her part in the economic and industrial development of the continent as well as in the intellectual movement which is doing so much to draw the two Americas together.

#### REGULATIONS FOR ENFORCEMENT OF SO-CALLED NET WEIGHT LAW

The regulations for the carrying out of the so-called Net Weight Law, which compels manufacturers to make a clear statement of the weight, volume, or contents of their packages of food, were signed May 11th by the Secretaries of the Treasury, Agriculture, and Commerce. The regulations as signed become effective at once, although the law, passed March 3, 1913, as an amendment to the Food and Drugs Act, defers the exacting of penalties for violations until September 3, 1914.

These regulations apply to foods shipped in interstate commerce or sold in the District of Columbia or the territories and, in general, require that the manufacturer of foods shall plainly mark all packages, bottles or other containers holding more than 2 ounces avoirdupois, or more than 1 fluid ounce, to show the net weight or volume of the contents. The volume of liquids must be computed at 68° F. The quantity stated on the container must represent the actual quantity of food exclusive of wrappings and container.

In general, solids must be stated in terms of weight and liquids in terms of volume, except that where there is a definite trade custom otherwise any marking of the package in terms that are generally understood to express definite quantities will be permitted.

The regulations also permit the statement of minimum volume or weight as "Minimum weight, 12 ounces," "Minimum volume, 1 gallon," "Not less than 4 ounces." In such cases the amount stated must approximate the actual quantity. No variations below the stated minimum quantity will be permitted.

#### TOLERANCES

In the packing and bottling of many foods, it would be impossible, or else add unnecessarily to cost, for the manufacturer to place an absolutely accurate statement of the amount of the food in every package, and for this reason the regulations permit tolerances or variations in packages where the discrepancies are due exclusively to unavoidable errors in weighing, measuring, or counting which occur in packing conducted in compliance with good commercial practice. This tolerance is allowed in order to permit the use of weighing and measuring machines which, like human operators, cannot weigh or measure every package with absolute accuracy. The regulations, however, provide that a run of such packages must show as many cases of overweight and as much excess as it does cases of underweight or undervolume.

Because goods shipped from one part of the country to another lose in weight by natural evaporation due to differences of atmospheric condition or temperature, tolerances will be allowed for such changes. The proper tolerances to be allowed will be determined on the facts in each case, and it is probable that the Department will establish tolerances for evaporation for various foods.

Packages containing 2 ounces avoirdupois or 1 fluid ounce of food, or less, are considered small, and are exempted from marking in terms of weight since providing accurate small bottles

and accurately measuring their contents in the case of a number of articles sold in small packages for 5 to 20 cents would be prohibitive in cost to the manufacturers and would force them to raise the price for the package or to put less food in it for the same price.

#### RUSSIAN TRADE IN FERTILIZERS IN 1913

International unrest caused great uncertainty in the fertilizer market in Russia during 1913, and the decreased demand embarrassed both wholesalers and retailers. Instead of the previous yearly increase of 20 per cent in the use of fertilizer, the consumption remained the same as in the previous year, and indeed, for some kinds of fertilizer (e. g., saltpeter) it decreased.

*Chemie* in its issue for March 28, 1914, gives the following data:

RUSSIAN FERTILIZER IMPORTS (TONS)	1912	1913
Natural phosphates.....	52,128	58,878
Basic slag (Thomas meal).....	202,518	202,968
Superphosphates.....	206,838	202,968
Stassfurt salts.....	91,296	84,582
Potassium chloride and sulfate.....	6,642	3,744
Chile saltpeter.....	56,718	47,646
Potassium nitrate and nitrite.....	2,466	2,556

#### NATURAL GAS IN HUNGARY

Until recently little capital had been invested in natural gas in Hungary, but the beginning of large scale operations came when an enormous gas supply was accidentally discovered at a depth of 990 ft. in a search for potash at Kissármás near Sármas in April, 1909. The gas which is nearly pure methane has kept up its pressure since then at 28-32 atmospheres, and the amount delivered daily in this region is estimated at about 6,000,000 cubic feet, *Chem. Ztg.*, 38 (1914), 469.

The nearest large cities which offer a market for this gas for power and illumination are Klausenburg and Maros Vásharhely about 62 miles away; a much larger undertaking than a line to these cities is however being considered, for a line to Budapest, 250 miles distant is projected. Even with this expensive overland line, which is to be modeled on the American pattern, it is believed that natural gas can offer keen competition in the capital. The fact that the gas wells are located in a country with little water makes their local commercial utilization difficult, although a small beginning in this direction has been made in lighting the trains of the state railway.

In March, a 45-mile pipe line, the longest in Europe, was opened from Kissármás to Torda and thence to Marosujvár. The pipes, of drawn steel, are from 20 to 45 feet long and 5 to 10 inches in diameter. They are joined with a special rubber packing, are covered with pitch and cased in an asphalt-jute coating. The country through which the line is laid offered great difficulties—among others frequent land slides; the cost of the line was in the neighborhood of \$700,000.

The "Methana" Erdgas-Studiengesellschaft has been organized in Budapest to study the chemical possibilities of the situation, for in the gas country there are rich supplies of mineral products; the problem of manufacturing nitric acid from the air by the Bender process is also being studied.

In the northwestern part of Hungary too, a supply of gas, accompanied here with oil, was discovered as recently as the end of 1913. The first well is yielding 1½ carloads of oil a day and about 17,000 cubic feet of gas (95 per cent methane) are given off hourly.

## SCIENTIFIC SOCIETIES

### INDUSTRIAL CHEMISTS AND CHEMICAL ENGINEERS DIVISION—REPORT OF PROGRESS BY COMMITTEE ON QUALITY OF PLATINUM LABORATORY UTENSILS, APRIL 9, 1914

The Committee on Quality of Platinum Laboratory Utensils submits the following report of progress, the first of a formal

character since the preliminary report published in *THIS JOURNAL*, 3 (1911), 686:

The committee itself has been unable to do more than to continue for a time the line of experimental work described in the report above referred to. The results are confirmatory in general of those already reported and need not be set forth in de-

tail here. The main reason for the long delay in securing data of sufficient importance to communicate formally has been due to the difficulties encountered in devising suitable means for accurately determining the volatility losses suffered by commercial ware when subjected to the temperatures ordinarily employed in laboratory operations. These difficulties have been, it is hoped, overcome through the assistance of the Heat and Metallurgical Divisions of the Bureau of Standards, and it is expected, as opportunity permits, to accumulate data of value.

There is, however, another more serious difficulty arising from the fact that the committee has been unable to obtain reliable information on the composition of much of the ware which is at its disposition, either through loan or purchase. Until exact data of this kind are available it will be difficult, if not impossible, to determine all the causes of poor quality in ware or to explain certain differences observed in the behavior of ware from different sources. This information, it is realized, is not to be had from the makers, but can be gained only by carrying out an elaborate investigation involving the preparation of pure metals and of some of their alloys and also by the careful analysis of commercial ware. It is hoped that in time the Bureau of Standards may be able to take up such an investigation, which it is quite impossible for the committee to assume. This Division, or better still the Society, could lend most valuable support to a project of this kind by urging upon the proper authorities the great need for a thorough study of the platinum metals and their alloys, a study which will involve the expenditure of a considerable sum of money. The investigation should not be restricted to a study of the subject from the point of view of the chemist alone, but should be made comprehensive as to the physical constants and physical behavior of the metals and alloys, so that all users of the platinum metals might benefit.

In the meantime, however, Dr. G. K. Burgess, of the Bureau of Standards, assisted by Mr. P. D. Sale, has developed a method for determining with exactness and rapidity the total impurity in any platinum alloy in terms of iridium, which is the most common associate of platinum in commercial ware. This method depends upon the measurement of the electromotive force of the alloy against pure platinum at a given temperature. So far the method has shown itself very reliable for platinum containing known amounts of iridium, and its application will be extended, if suitable materials can be obtained, to other binary alloys of platinum and its common associates. At present it is not possible to determine what other metal or metals may be alloyed with platinum, but, as said above, their joint effect can be given in terms of iridium. The determination takes but a few minutes. The method is printed in full in this issue (p. 452) in the form of a paper by Messrs. Burgess and Sale, with the results obtained on the various samples loaned to our committee by American manufacturers, of platinum ware, as well as upon articles of English, German and French make and some purchased specimens of American make.

Since this work is a direct outcome of the activity of our committee, we feel that substantial progress has been made, notwithstanding that we have no experimental data of importance to present on our own immediate behalf, and we take this opportunity to express to Messrs. Burgess and Sale and to the Director of the Bureau of Standards our appreciation of their efforts to forward our work.

It was hoped that, after the publication of our first report, American manufacturers would furnish to purchasers commercial ware of decidedly better quality, as to iron and perhaps other base metal content, than they had been offering in recent years. This hope has proved illusory as to some at least of the ware now sold, so far as we can judge from specimens recently submitted for test at the Bureau of Standards, on request of one of us.

In order that more information may be acquired as to the quality of ware sold from now on, the committee asks purchasers to submit to it one or two specimens (particularly crucibles) from each lot of new and unused ware. The committee is authorized to say that these samples will be examined at the Bureau of Standards (for the present without charge) in such manner as not to injure the articles, and reports will be made to the senders. The tests will be directed, so far as can now be foreseen, toward the detection of iron or other base metal (as shown in part by the appearance of the surface of the ware after ignition) and to the determination of the sum of alloyed metals in terms of iridium by the thermoelectric method above mentioned. The determination of loss on prolonged heating at high temperatures will not, for the present, figure in the tests. The Bureau will reserve the right to make such use of the results of its examination as it may find desirable.

It is believed that the adoption of this course by a sufficiently large number of users of platinum utensils, during the next few years, will bring about speedy improvement in the quality of commercial ware. If not, the committee will probably make other recommendations for the protection of the public.

W. F. HILLEBRAND  
E. T. ALLEN  
PERCY H. WALKER

#### AMERICAN CHEMICAL SOCIETY—49th MEETING, CINCINNATI, APRIL 6-10, 1914

##### FERTILIZER CHEMISTRY DIVISION REPORT

The meeting was called to order by Mr. J. E. Breckenridge, Chairman. After the transaction of the usual routine business, the papers were presented as published in the official program.

An amendment to the by-laws was adopted, making a general Committee on Research and Methods of Analysis in place of the Committees on Nitrogen, Phosphoric Acid, Phosphate Rock and Potash.

The meeting was very well attended considering the conditions which would enforce the absence of a good many of the members at this season of the year.

F. B. CARPENTER, *Secretary*

##### REPORT OF THE COMMITTEE ON FERTILIZER LEGISLATION

The question of uniform fertilizer legislation having occupied the attention of this division for some time, the following resolution adopted by the Association of Southern Agricultural Workers at the annual meeting in Montgomery, Ala., Feb. 26th, will be of interest:

"WHEREAS, the wide variation in the requirements now existing in our Southern States for the branding of fertilizer packages are a source of confusion to purchasers, a waste of time and liability to errors in inspection, and an unnecessary expense to manufacturers,

"THEREFORE, BE IT RESOLVED, that this Association endorses uniformity and simplicity in branding, and urges the officials in charge of fertilizer control in our Southern States to use their influence in securing such legislation as will bring about simplicity and uniformity in branding of commercial fertilizers."

Your committee was represented at this meeting and participated in the discussion.

In the matter of new legislation there have been a few minor changes since the last report, but not of such a nature as to materially affect either the manufacturer or consumer.

F. B. CARPENTER, *Chairman*

##### REPORT OF COMMITTEE ON PHOSPHORIC ACID

This Committee has been asked to prepare a résumé of the work done since its organization, for the guidance of the Committee on Methods of Analysis.

This Committee first turned its attention to the determination



of insoluble phosphoric acid, since it thought a method which would give more concordant results was needed.

Since there are several factors which influence the determination of insoluble, such as the neutrality of the ammonium citrate, time required for filtering insoluble, etc., the best way of attacking the problem seemed to be to vary one of the factors at a time, keeping the others constant.

The first question taken up was the preparation of neutral ammonium citrate. A solution of citrate was prepared by one of the members of the Committee, and sent out with the samples. Those to whom samples were sent were asked to prepare a citrate solution and run samples with the solution prepared by them and also with that sent out by the Committee.

The results<sup>1</sup> showed that it was possible to prepare a solution which would give results which were the same as those obtained by the Committee citrate, but results from different analysts showed great variation between them. One of the chief causes of this great variation was due to the great difference in time required for filtration.

Another set of samples was prepared and together with these samples was sent a standard sample on which the Committee had determined the total phosphoric acid.

The total in standard sample ran about the same as the highest insoluble. The instructions which accompanied were the same as those sent out with the previous lot of samples, except that the method of filtration was shortened by transferring the precipitate to another filter in cases where filtration was difficult. The results<sup>2</sup> showed some improvement in the case of goods difficult to filter, but in the case of acid phosphate the variation between analysts was the same.

The results obtained on the last set of samples are somewhat disappointing. The differences do not follow any rule, hence it is difficult to assign any reason for the variation. The most probable cause of the variations is due to the failure, on the part of the analyst, to observe the details of the method closely. Analysts who have had considerable experience with the method think that much better results should be obtained where the details of the method are closely observed.

J. Q. BURTON  
COMMITTEE W. J. JONES  
J. R. POWELL  
G. FARNHAM, *Chairman*

## REPORT OF THE ANALYTICAL COMMITTEE—RUBBER SECTION AMERICAN CHEMICAL SOCIETY

[The following report was presented to the Rubber Section of the A. C. S. at Cincinnati on April 8, 1914, and the Section authorized its publication for the purpose of bringing the results obtained to the attention of those interested in the work and in answer to the Joint Rubber Insulation Committee's request for criticisms. DORRIS WHIPPLE, *Secretary*.]

Your Committee begs to present herewith the third report of the investigations made by this Committee, together with the results obtained.

The major part of the work of this Committee has been confined to certain methods of procedure as outlined by the *Joint Rubber Insulation Committee* for the analysis of materials used for insulating purposes. The results obtained on previous work were presented to the members of the Rubber Section at the Milwaukee meeting and at the Rochester meeting. The Committee has not included the previous work in the present report (although the same has a direct bearing on the present report) as some of the methods have been changed or revised. In the time intervening between the Rochester meeting and the present day, this Committee has investigated the completed preliminary procedure of the *Joint Rubber Insulation Committee* and these final results are the ones tabulated below.

<sup>1</sup> This JOURNAL, 3 (1911), 118.  
<sup>2</sup> *Ibid.*, 6 (1913), 956.

The determinations as reported herewith were made on three samples which were prepared and averaged with the greatest care by Mr. G. H. Savage and the formulas used by him are given below in detail in as much as it has a direct bearing on the present report.

The various ingredients which went to make up these three compounds were weighed with extreme accuracy and compounded with the greatest care in order that uniform average samples might be obtained. The vulcanized compounds were then ground according to the requirements of the procedure under investigation, carefully mixed and placed in small vials which held the approximate amount required for the various determinations. These were sent by express to the various members and the analysis on the first determination started by each member within approximately twenty-four hours of the time of grinding the sample. These samples were re-analyzed at intervals as indicated in the report.

This Committee respectfully refers the members of the Rubber Section to THIS JOURNAL, 6, 75, for the complete method of procedure of the *Joint Rubber Insulation Committee* as followed by this Committee in the analysis of the three samples prepared by Mr. Savage.

The formulas of the three compounds, together with the analytical results obtained, are tabulated below.

### FORMULAS USED IN PREPARING COMPOUNDS ANALYZED

	A	B	C
Fine Paraffin.....	297	309	324
Hard Paraffin.....	25		
Ceresine.....		25	
Sulfur.....	19	19	19
Litharge.....	70	70	70
Zinc Oxide.....	350	350	350
Whiting.....	239	227	237
	1000	1000	1000

No corrections, additions or omissions have been made in reporting these analytical results. The analysts' numbers refer to the following: 1—E. W. Boughton; 2—D. W. Whipple; 3—W. A. Ducca; 4—G. H. Savage; 5—J. B. Tuttle.

### SAMPLE A—FIRST ANALYSIS

Analyst's No.....	1	1	2	2	3	4	4	5
Date of Extraction with Acetone.....	11/13	11/15	11/14	11/20	11/20	11/13	11/13	11/13
Total Acetone Extract (%).....	4.16	4.12	3.97	4.03	4.18	3.84	3.78	4.08
Free Sulfur (%).....	0.87	0.86	0.80	0.82	0.90	0.70	0.66	0.87
Unsaponifiable Material (%).....	2.97	2.70	2.76		3.29	2.71	2.69	2.69
Waxy Hydrocarbon A (%).....	2.29	2.25	2.18		2.27	2.39	2.31	2.40
Waxy Hydrocarbon B (%).....	0.34	0.20	0.32		0.56	0.14	0.20	0.11
Total Waxy Hydrocarbon By Difference (%).....	2.63	2.45	2.50		2.83	2.53	2.51	2.54
Organic Extract (%).....	3.29	3.26	3.17	3.21	3.28	3.14	3.12	3.26
Saponifiable Acetone Extract (%).....	0.32	0.56	0.41			0.43	0.43	0.87
Unsaponifiable Resins (%).....	0.34	0.25	0.26			0.18	0.18	

### SAMPLE A—SECOND ANALYSIS

Analyst's No.....	1	1	2	2	3	4	4	5
Date of Extraction with Acetone.....	11/20	11/21	11/25	11/23	12/4	11/20	11/20	11/20
Total Acetone Extract (%).....	4.13	4.16	4.14	4.02	3.72	3.90	4.00	4.20
Free Sulfur (%).....	0.88	0.79	0.88	0.80	0.89	0.65	0.65	0.91
Unsaponifiable Material (%).....	2.32	2.75	2.82	2.81	2.54	2.41	2.51	2.60
Waxy Hydrocarbon A (%).....	1.97	2.31	2.31	2.37	2.32	2.11	2.32	2.51
Waxy Hydrocarbon B (%).....	0.17	0.24	0.25	0.19	0.49	0.10	0.10	0.11
Total Waxy Hydrocarbon By Difference (%).....	2.55	2.64	2.56	2.56	2.81	2.21	2.42	2.62
Organic Extract (%).....	3.25	3.37	3.26	3.22	2.83	3.25	3.35	3.29
Saponifiable Acetone Extract (%).....	0.93	0.62	0.44	0.41	0.29	0.84	0.84	0.69
Unsaponifiable Resins (%).....	0.18	0.20	0.26	0.25				0.09
Fillers (%) Sulfur-free.....		70.7		71.6(a)		72.68	73.75	71.1

(a) This determination was not made by the same analyst.

Analyst's No.	SAMPLE A—THIRD ANALYSIS								
	1	1	2	2	3	4	4	5	
Date of Extraction with Acetone.....	12/4	12/5	12/9	12/12		12/4	12/4	12/4	
Total Acetone Extract (%).....	4.08	4.06	3.97	3.97		4.08	4.01	4.28	
Free Sulfur (%).....	0.82	0.87	0.80	0.83		0.72	0.75	0.96	
Unsaponifiable Material (%).....	2.81	2.77	2.84	2.73		2.78	2.80	2.68	
Waxy Hydrocarbon A (%).....	2.30	2.25	2.30	2.30		2.42	2.41	2.43	
Waxy Hydrocarbon B (%).....	0.34	0.28	0.17	0.14		0.11	0.16	0.11	
Total Waxy Hydrocarbon (%).....	2.64	2.53	2.47	2.44		2.53	2.57	2.54	
By Difference.....									
Organic Extract (%).....	3.26	3.19	3.17	3.14		3.36	3.26	3.32	
Saponifiable Acetone Extract (%).....	0.45	0.42	0.33	0.41		0.58	0.46	0.64	
Unsaponifiable Resins (%).....	0.17	0.24	0.37	0.29		0.25	0.23		

SAMPLE B—FIRST ANALYSIS

Analyst's No.	SAMPLE B—FIRST ANALYSIS								
	1	1	2	2	3	4	4	5	
Date of Extraction with Acetone.....	11/13	11/5	11/14	11/20		11/13	11/13	11/14	
Total Acetone Extract (%).....	4.04	3.95	3.92	3.85		3.70	3.73	4.24	
Free Sulfur (%).....	0.73	0.80	0.75	0.67		0.53	0.56	0.86	
Unsaponifiable Material (%).....	2.54	2.59	2.82	2.67		2.65	2.63	2.55	
Waxy Hydrocarbon A (%).....	1.94	2.05	2.08	2.09		2.15	2.18	2.23	
Waxy Hydrocarbon B (%).....	0.29	0.27	0.36	0.17		0.22	0.25		
Total Waxy Hydrocarbon (%).....	2.23	2.32	2.44	2.26		2.37	2.43		
By Difference.....									
Organic Extract (%).....	3.31	3.15	3.17	3.18		3.17	3.17	3.38	
Saponifiable Acetone Extract (%).....	0.77	0.56	0.35	0.51		0.52	0.54	0.83	
Unsaponifiable Resins (%).....	0.31	0.27	0.38	0.41		0.28	0.20		

SAMPLE B—SECOND ANALYSIS

Analyst's No.	SAMPLE B—SECOND ANALYSIS								
	1	1	2	2	3	4	4	5	
Date of Extraction with Acetone.....	11/20	11/21	11/24	11/25	11/20	11/20	11/20	11/20	
Total Acetone Extract (%).....	4.04	4.04	4.01	3.92	4.30	4.00	3.95	4.23	
Free Sulfur (%).....	0.80	0.81	0.77	0.73	0.97	0.73	0.69	0.85	
Unsaponifiable Material (%).....	2.54	2.52	2.74	2.70	2.73	2.11	2.56	2.58	
Waxy Hydrocarbon A (%).....	2.02	1.95	2.24	2.28	2.20	1.91	2.09	2.39	
Waxy Hydrocarbon B (%).....	0.23	0.34	0.20	0.26	0.64	0.14	0.16		
Total Waxy Hydrocarbon (%).....	2.25	2.29	2.44	2.52	2.84	2.05	2.25		
By Difference.....									
Organic Extract (%).....	3.24	3.23	3.24	3.19	3.33	3.27	3.26	3.38	
Saponifiable Acetone Extract (%).....	0.70	0.71	0.50	0.49	0.60		0.70	0.80	
Unsaponifiable Resins (%).....	0.29	0.23	0.30	0.18			0.31		
Fillers (%).....	67.8	71.6(a)				74.80	72.85	69.3	

(a) This determination was not made by the same analyst.

SAMPLE B—THIRD ANALYSIS

Analyst's No.	SAMPLE B—THIRD ANALYSIS								
	1	1	2	2	3	4	4	5	
Date of Extraction with Acetone.....	12/4	12/5	12/9	12/12	12/4	12/4	12/4	12/4	
Total Acetone Extract (%).....	4.03	3.95	3.86	3.94	3.75	4.00	3.98	4.12	
Free Sulfur (%).....	0.88	0.78	0.73	0.75	0.57	0.92	0.71	0.79	
Unsaponifiable Material (%).....	2.71	2.78	2.72	2.61	2.36	2.69	2.61	2.57	
Waxy Hydrocarbon A (%).....	2.26	2.08	2.10	2.10	2.18	2.31	2.22	2.32	
Waxy Hydrocarbon B (%).....	0.21	0.47	0.28	0.22	0.54	0.11	0.18		
Total Waxy Hydrocarbon (%).....	2.47	2.53	2.38	2.32	2.72	2.42	2.40		
By Difference.....									
Organic Extract (%).....	3.15	3.17	3.13	3.19	3.18	3.08	3.27	3.33	
Saponifiable Acetone Extract (%).....	0.44	0.39	0.41	0.58	0.82	0.39	0.66	0.76	
Unsaponifiable Resins (%).....	0.24	0.25	0.34	0.29		0.27	0.21		

SAMPLE C—FIRST ANALYSIS

Analyst's No.	SAMPLE C—FIRST ANALYSIS								
	1	1	2	2	3	4	4	5	
Date of Extraction with Acetone.....	11/13	11/15	11/14	11/20	11/20	11/13	11/13	11/14	
Total Acetone Extract (%).....	1.55	1.44	1.48	1.40	1.72	1.15	1.09	1.58	
Free Sulfur (%).....	0.79	0.76	0.74	0.70	0.89	0.52	0.55	0.85	
Unsaponifiable Material (%).....	0.25	0.22	0.18	0.26	0.60	0.51	0.44	0.17	
Waxy Hydrocarbon A (%).....					0.63				
Waxy Hydrocarbon B (%).....	0.09	0.05	0.05	0.06		0.18	0.11		
Total Waxy Hydrocarbon (%).....									
By Difference.....									
Organic Extract (%).....	0.76	0.68	0.74	0.70	0.83	0.63	0.54	0.73	
Saponifiable Acetone Extract (%).....	0.51	0.46	0.56	0.44	0.23	0.12	0.10	0.56	
Unsaponifiable Resins (%).....	0.16	0.17	0.13	0.20		0.33	0.33		

Analyst's No.	SAMPLE C—SECOND ANALYSIS								
	1	1	2	2	3	4	4	5	
Date of Extraction with Acetone.....	11/20	11/21	11/25	12/4		11/20	11/20	11/20	
Total Acetone Extract (%).....	1.52	1.58	1.47	1.47		1.39	1.40	1.74	
Free Sulfur (%).....	0.81	0.77	0.76	0.74		0.67	0.69	0.83	
Unsaponifiable Material (%).....	0.26	0.27	0.15	0.18		0.10	0.11	0.17	
Waxy Hydrocarbon A (%).....									
Waxy Hydrocarbon B (%).....	0.06	0.06	0.05	0.05		0.05	0.05		
Total Waxy Hydrocarbon (%).....	0.06	0.06	0.05	0.05		0.05	0.05		
By Difference.....									
Organic Extract (%).....	0.71	0.81	0.71	0.73		0.72	0.71	0.91	
Saponifiable Acetone Extract (%).....	0.45	0.54	0.56	0.55		0.62	0.60	0.74	
Unsaponifiable Resins (%).....	0.20	0.21	0.10						
Fillers (%).....	71.8		71.4(a)			74.1	75.43	70.7	

(a) This determination was not made by the same analyst.

SAMPLE C—THIRD ANALYSIS

Analyst's No.	SAMPLE C—THIRD ANALYSIS								
	1	1	2	2	3	4	4	5	
Date of Extraction with Acetone.....	12/4	12/5	12/9	12/12	12/4	12/4	12/4	12/4	
Total Acetone Extract (%).....	1.49	1.44	1.34	1.47	1.19	1.44	1.42	1.62	
Free Sulfur (%).....	0.80	0.79	0.70	0.76	0.79	0.67	0.67	0.82	
Unsaponifiable Material (%).....	0.22	0.28	0.25	0.20	0.23	0.35	0.31	0.15	
Waxy Hydrocarbon A (%).....					0.29				
Waxy Hydrocarbon B (%).....	0.06	0.06	0.05	0.08		0.07	0.05		
Total Waxy Hydrocarbon (%).....	0.06	0.06	0.05	0.08		0.07	0.05		
By Difference.....									
Organic Extract (%).....	0.69	0.65	0.64	0.71	0.40	0.77	0.75	0.80	
Saponifiable Acetone Extract (%).....	0.47	0.37	0.39	0.51	0.17	0.42	0.44	0.65	
Unsaponifiable Resins (%).....	0.16	0.22	0.17	0.12		0.28	0.26		

At a meeting of the Analytical Committee held in Washington on March 20, 1914, the undersigned members of the Committee unanimously agreed to report to the Rubber Section and to those interested in the work, the following recommendations:

1—The results of our investigations have shown that the determinations of acetone extract, free sulfur, total waxy hydrocarbons and total sulfur are sufficiently accurate and reliable to warrant our endorsement.

2—The results of our investigations have shown that the determination of fillers is inaccurate and unreliable and therefore the calculation of the amount of rubber as prescribed by this procedure is equally inaccurate and unreliable.

3—The results of our investigations have shown that the contributing steps for the division of resins into saponifiable and unsaponifiable resins are inaccurate and unreliable; therefore, the sum of the two should be reported as resins present and no division of resins indicated.

E. W. BOUGHTON      J. B. TUTTLE  
W. A. DUCCA          P. H. WALKER  
G. H. SAVAGE          D. W. WHIPPLE, *Chairman*

#### COMMENTS OF JOINT RUBBER INSULATION COMMITTEE ON REPORT OF ANALYTICAL COMMITTEE OF RUBBER SECTION OF THE AMERICAN CHEMICAL SOCIETY, APRIL 8, 1914

The Joint Rubber Insulation Committee desired criticisms of its preliminary report that inaccuracies may be corrected before the final report is issued, and wishes to thank the Analytical Committee for the work it has undertaken in this connection. The publication of the results of the Analytical Committee has been authorized by the Rubber Section. In spite of this, a close examination of these results shows their value to be doubtful.

The Analytical Committee has drawn conclusions from results of this and its previous reports and has endorsed four of the determinations, namely, the acetone extract, free sulfur, waxy hydrocarbons and total sulfur. The chloroform extract and the alcoholic potash extract have not been criticized.

The report draws two other conclusions from the data pub-

lished, one of which concerns the determination of fillers and the other, the division of resins into saponifiable and unsaponifiable.

There has been but one compound analyzed, of which there are three variations: one with paraffin, one with ceresin and one without waxy hydrocarbons. We understand that these were made from the same lot of raw rubber. They contain practically the same percentages of the various mineral ingredients, so that the determinations of fillers and of resins are practically a repetition of the determinations of one compound. The Analytical Committee draws general conclusions as to the value of these determinations from the results on this one compound.

No data are given on the raw rubber and we cannot judge whether it contained the normal amount of insoluble matter. From the tables of the Analytical Committee it appears that all the results on fillers are too high. It is possible that the compound used may have certain characteristics which magnify the errors of the determination. It is known to the Committee that errors may occur and the subject is being investigated. It has been the experience of the Committee that the magnitude of these errors is less after practice with the procedure.

We have assumed above that all members of the Analytical Committee followed the prescribed procedure absolutely. An examination of the results on the different constituents of the acetone extract indicates that the procedure has not been followed by all the members of the Analytical Committee.

In this connection we would like to call attention to the following note in the tentative report of this Committee (THIS JOURNAL, 6, 81): "With a procedure of this length, it is impossible to explain every detail without undue elaboration and the Committee wishes to point out that while to experienced chemists the procedure may seem overburdened by detail, yet every specified detail was found necessary in order that the conditions essential to accurate and consistent work might be reproduced by all chemists using the procedure. For this reason it is extremely important that all instructions be observed even if their significance is not perceived by the individual chemist. It will probably be found that even with the instructions properly observed, some experience will be needed to apply the method successfully."

The results given for Compound A (11/20 and 11/21) under No. 1 on Total Waxy Hydrocarbons, contain what may be assumed to be a clerical error. However, in all the results given under No. 3 we can find no clerical error to account for the absurdity of the results. For instance, in every case but one there is a greater value given for total waxy hydrocarbons than for unsaponifiable material, which, according to the procedure, is an absolute impossibility. We do not attempt to explain the results, but we do point out that the results are necessarily in error and cannot be considered in judging the procedure.

The results under No. 4 for total acetone extract and free sulfur are consistently low. If the results under Nos. 1, 2 and 5 are averaged and compared with the average results obtained by No. 4, it will be seen that the lower results on free sulfur probably account for the lower acetone extract of No. 4.

Sample A	Act. Exl.	Free S.	Act. Exl.	Free S.	Act. Exl.	Free S.
Av. Nos. 1, 2 and 5.....	4.07	0.83	4.13	0.85	4.07	0.86
Av. No. 4.....	3.81	0.68	3.95	0.65	4.05	0.74
Difference.....	0.26	0.15	0.18	0.20	0.02	0.12
Sample B						
Av. Nos. 1, 2 and 5.....	4.00	0.76	4.05	0.79	3.98	0.79
Av. No. 4.....	3.72	0.55	3.98	0.71	3.99	0.82(a)
Difference.....	0.28	0.21	0.07	0.08	-0.01	-0.03
Sample C						
Av. Nos. 1, 2 and 5.....	1.49	0.77	1.56	0.78	1.47	0.77
Av. No. 4.....	1.12	0.54	1.40	0.68	1.43	0.67
Difference.....	0.37	0.23	0.16	0.10	0.04	0.10

(a) Very poor checks

These results indicate that the acetone extraction was not properly made. The Committee believes that the prescribed form of extraction apparatus was not used, and that used would

account for the loss of free sulfur and the consequent lower acetone extract.

Another apparent discrepancy in the results can be explained on close examination. If we average all the results on saponifiable acetone extract, obtained by Nos. 1, 2, 4 and 5, on each variation of the compound analyzed, we obtain the following:

AVERAGE SAPONIFIABLE ACETONE EXTRACT				
Analyst's No.	1	2	4	5
Sample A.....	0.55	0.40	0.60	0.63
Sample B.....	0.60	0.48	0.66	0.79
Sample C.....	0.47	0.50	0.52(a)	0.65

(a) Eliminating results of 0.10 and 0.12, 11/13, obviously in error.

The averages given under No. 2, on Samples A and B are lower than those obtained by Nos. 1, 4 and 5, and on examination of the acetone extracts obtained by No. 2, it will be seen that he obtained consistently lower results than Nos. 1, 2 and 5. The results indicate that the acetone extraction was not properly made and that this has probably caused lower saponifiable resins. If we, therefore, eliminate the results of No. 2, those obtained by Nos. 1, 4 and 5 for "A" and "B" are about what we would expect from this compound. When we come to results for "C," we do not see how any conclusions can be drawn.

The object of the separation of the resins into saponifiable and unsaponifiable was to differentiate between different rubbers, and we are sorry that the Analytical Committee did not investigate other rubbers in order to show the differences between them.

Considering the results as a whole we are of the opinion that the report of the Analytical Committee would have had more bearing on the procedure under consideration if that procedure had been carefully followed.

We hope that the work of the Analytical Committee will lead to other criticisms in order that we may avail ourselves of the experience gained this year, and incorporate whatever improvements we may decide upon in a later report.

JOINT RUBBER INSULATION COMMITTEE  
WM. A. DEL MAR, *Secretary*

April 29, 1914

## AMERICAN INSTITUTE OF CHEMICAL ENGINEERS 6th SEMI-ANNUAL MEETING, TROY, JUNE 17-20, 1914 PROGRAM OF PAPERS

1. Address of Welcome. HONORABLE C. F. BURNS, Mayor of Troy.
2. Presidential Address. M. C. WHITAKER.
3. The Saratoga Septic Tanks (Lantern). WM. P. MASON.
4. The Application of Physical Chemistry to Industrial Processes. W. F. RITTMAN.
5. Studies on Filtration. J. W. BAIN and A. E. WIGLE.
6. Scrubber for Vacuum Apparatus for Laboratories. CHARLES BASKERVILLE.
7. Shoddy and Carbonized Waste. L. J. MAYOS.
8. A Combination Water Softener and Storage Tank (Lantern). L. M. BOOTH.
9. The Present Patent Situation. M. TOCH.
10. Ozone and Ventilation. J. C. OLSEN and WM. H. ULRICH.
11. Bleaching Cotton Fiber. J. C. HEDDEN.
12. Development of Rotary Furnaces (Lantern). R. K. MEADE.
13. An Oil Shale from Nevada (Illustrated). CHARLES BASKERVILLE.

### EXCURSIONS

- Laboratories of Rensselaer Polytechnic Institute.  
U. S. Arsenal (Heavy Guns).  
Geo. P. Ide & Co. (Collars and Shirts).  
General Electric Co. Plant at Schenectady.  
Saratoga (The N. Y. State Reservation, the Springs and Sewage Disposal Plant).  
Water Works at Albany (Slow Sand Filter Beds and Mechanical Scrubbing Filters).  
West Virginia Pulp & Paper Co. Plant at Mechanicsville.  
Burden Iron Works (Puddling Process for Wrought Iron).  
Cohoes Filter Plant (Mechanical Filters).  
Freihoffer Baking Co.

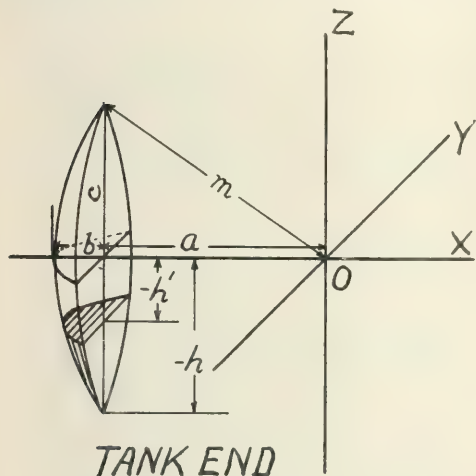


# NOTES AND CORRESPONDENCE

## FORMULA FOR CONTENTS OF CYLINDRICAL TANKS WITH SPHERICAL ENDS

Editor of the Journal of Industrial and Engineering Chemistry:

In most all chemical plants of any size many cylindrical tanks with spherical ends are used for liquids. To ascertain contents of these tanks by measuring the depth of the liquid inside, it is necessary to consult a curve representing the gallons per inch of depth. It is a comparatively simple matter to calculate the volume per inch of the main portion of the tank, but calculating that of the spherical ends is a more complicated problem.



The DuPont Fabrikoid Co., manufacturers of artificial leathers, use about ten of these cylindrical tanks with spherical ends. They are mostly of different sizes and I was given the task of plotting the necessary curves. I have worked out the following formula:

$$V = 2 \int_{-h}^{-h'} \int_a^m \sqrt{m^2 - x^2} \, dx \, dy$$

The limits are obtained from the equation of the sphere,  $x^2 + y^2 + z^2 = m^2$ , where  $m = \frac{c^2 + b^2}{2b}$ .

By integration and expansion,  $V = \left[ Az + Bz^3 + Cz^5 \right]_{-h}^{-h'}$

$$\text{where, } A = \frac{\pi}{2} m^2 \cdot am - \frac{a^3}{6m} - \frac{3a^5}{40m^3} \cdot am$$

$$B = \frac{a}{6m} - \frac{\pi}{6} - \frac{a^3}{36m^3} - \frac{3a^5}{80m^5} + \frac{a}{6m}$$

$$C = \frac{a}{40m^3} - \frac{a^3}{80m^5} - \frac{9a^5}{320m^7} + \frac{a}{40m^3}$$

Substituting the value of  $m/2$  for  $z$  in the formula, we obtain the volume in both ends of half the tank,  $V_{1/2}$ . By substituting  $h$ , the depth as measured for  $z$  in the formula and subtracting this volume,  $V_z$ , from  $V_{1/2}$ , we get the volume in the ends for the desired depth of liquid,

$V = V_{1/2} - V_z$ , or the formula becomes:

$$V = [A_2^m + B_2^m + C_2^m] - [Ah + Bh^3 + Ch^5]$$

L. E. CARPENTER

110 GRAND STREET, NEWBURGH, NEW YORK  
February 17, 1914

## NOTE ON INFLUENCE OF RATE OF STIRRING ON TITRE DETERMINATIONS IN FATS

Editor of the Journal of Industrial and Engineering Chemistry:

At the time that the official method now in use in determining the Titre of Fats was adopted, it was noted that the stirring method, *i. e.*, continuous stirring of the fatty acids until the temperature was stationary for 30 seconds, gave tests higher than if the fatty acid was cooled to the stopping point without stirring; this higher test ranged from over  $1^\circ$  C. in case of oils such as Cottonseed to only  $0.1^\circ$  or less in the case of Stearine.

Since this stirring method was adopted, the custom in this laboratory has been to stir the fatty acids by means of a stirrer run by a water-motor and it was soon noticed that the number of revolutions per minute of the fatty acids (the acids being revolved and the thermometer kept stationary) had a decided influence on the test. I give below a number of figures made in two different fats, the first being a Garbage Grease (Naphtha extracted) and the second a tallow:

	Revolutions per min	Stopping point	Final highest point
Garbage Grease	60	36.35	37.05
	80	36.50	37.20
	180	37.20	37.55
	220	37.40	37.65
Tallow	60	43.60	44.60
	80	42.70	44.50
	180	44.60	45.00
	220	44.60	45.00

It will be noticed that when the speed is only 60 revolutions the first stopping point is much lower than when it is 180 or 220, in fact, the less the speed the lower the first stopping point and as the speed is increased, the stopping point rises with each increase.

In the case of the tallow, the rate above 180 makes no difference with either temperature but with the grease a difference of  $0.1^\circ$  is noted. A quite remarkable difference in the first stopping point is noted in the tallow at 60 revolutions, although the final temperature is practically the same.

In my opinion, a large number of the differences between chemists on this test is due to this point. At the present time the directions state only that the acids "shall be stirred slowly," which might mean anything. I believe that a definite rate of stirring should be specified and my judgment is that 180 revolutions should be taken as the standard, as a higher rate is rather impracticable and a lower certainly does not give correct figures. As the titre point is the highest temperature recorded by the heat of crystallization of the fatty acids, any method that will give this highest heat should be the correct one, as it is obvious that the only source of heat is from the crystallizing. In fact, a higher rate of stirring would, if anything, tend to cool the acids and so give a low test.

A. G. STILLWELL

763 1/2 PINE ST., NEW YORK  
March 30, 1914

## A SHAKER FOR THE MECHANICAL ANALYSIS OF SOILS

Editor of the Journal of Industrial and Engineering Chemistry:

In an article in February, 1914, THIS JOURNAL, entitled "A Shaker for the Mechanical Analysis of Soil," by Freeman Ward, the author makes a comparison between the shaking machine devised by him and the one used by the Bureau of Soils. He states: "The writer believes that his method is better than the one used by the Bureau of Soils in two respects. In the first place, the machine is simple and inexpensive. A greater advantage is the saving of time. Clean separations can be effected in three hours, and in some cases two hours; this is a saving of at least four hours over the Bureau method. If the quantity of the water used in the bottles is reduced one-half, a clean separation results in much less than three hours, but there is a tendency for the grains to suffer some abrasion."

The machine is undoubtedly simple and inexpensive. Attention must be called to the fact, however, that the Ward apparatus carries only 16 bottles while the Bureau of Soils apparatus carries 48, giving the latter three times the capacity. The Ward shaker must be run at a certain definite speed to be efficient. If the speed is too high, there is a centrifugal effect resulting, and if too slow, the action is merely pouring. The Bureau of Soils machine is even more efficient at high speeds than at moderate speeds.

As to the second conclusion, that a saving of time results, the author has taken the statement in Bureau of Soils Bulletin No. 84 that the samples of soil are "shaken by the mechanical shaking machine for at least seven hours," to mean that seven hours are essential. As a matter of fact, this time is taken because in some rare instances as long a time as this has been found necessary. A majority of soils, especially sandy soils, do not need seven hours. The length of time of shaking does not result in any loss of time to the operator, as the analyst merely keeps 48 soils shaking on the machine all the time and cannot complete the analyses rapidly enough with a force of three men to keep the machine cleared of samples ready for analysis. If more samples should be required, all that is necessary is to run the machine during the night, and thus the capacity of the machine would be doubled.

In the light of these facts, it seems to the writer that Mr. Ward's statement that his "method is better than the one used by the Bureau of Soils" is misleading. A more accurate claim would be that his machine is satisfactory where such a small amount of work is done as to preclude buying an expensive piece of apparatus. His machine can be cheaply constructed and is greatly superior to pestling.

C. C. FLETCHER

BUREAU OF SOILS  
U. S. DEPARTMENT OF AGRICULTURE, WASHINGTON  
February 24, 1914

#### A NOTE ON THE QUANTITY OF BENZOIC ACID CONTAINED IN PRUNES AND CRANBERRIES

*Editor of the Journal of Industrial and Engineering Chemistry:*

Although it is well recognized that certain fruits contain relatively large amounts of benzoic acid or its salts, data specifically stating the exact quantities are not numerous. In connection with work in progress in this laboratory, it became desirable to determine the quantity of benzoic acid in prunes and in cranberries.

For the estimation of benzoic acid the method of Krüger (*Zeitschr. f. Untersuch. d. Nahr. u. Genussmittel*, 1913, July) was employed, 50 grams of fruit being taken for a determination.

From several duplicate analyses in each instance it was found that prunes as obtained in the market contained approximately 0.05 per cent benzoic acid. Cranberries have a somewhat higher benzoate content, benzoic acid to the extent of 0.06 per cent being found.

These results were furnished from the weight of sublimed

benzoic acid and by titration—the data in each instance agreeing closely.

MORRIS J. RADIN

SHEFFIELD LABORATORY OF PHYSIOLOGICAL CHEMISTRY  
YALE UNIVERSITY, NEW HAVEN, CONN.  
March 7, 1914

#### BUREAU OF STANDARDS' ANALYZED SAMPLES

The Bureau of Standards is prepared to issue purified dextrose as a standard reducing sugar. The substance is free from ash and contains less than 0.1 per cent of moisture. In an atmosphere of average humidity it is slightly hygroscopic, but if dried at 70° C., it retains less than 0.01 per cent of moisture. A certificate of analysis showing the quantity of remaining impurity accompanies the sample. The purpose of the standard is to assist in the unification of reducing sugar analysis by supplementing or replacing the use of invert sugar. It is, also, available for general sugar work. Further information may be obtained in Circular 25 on Standard Samples or Circular 44 on Polarimetry.

FEES—Payable in advance: \$2 for 70 grams or \$3 for 140 grams.

#### PLATINUM THEFTS

*Editor of the Journal of Industrial and Engineering Chemistry:*

The following pieces of platinum have been stolen from the Chemical Laboratories of the University of Kansas:

CRUCIBLES		CRUCIBLES		DISHES	
No.	Approx. wt.	No.	Approx. wt.	No.	Approx. wt.
3	12 grams	4	12 grams	6	20 grams
7	12 grams	10	11 grams	7	20 grams
27	8 grams	25	12 grams	24	24 grams
1	11 grams	33	13 grams	25	25 grams
5	12 grams				

All persons are warned against purchasing any of these pieces. The ownership of scrap platinum should be fully traced before the scrap is purchased. Any information leading to the recovery of this material will be appreciated.

E. H. S. BAILEY, *Director of Chemical Laboratories*

UNIVERSITY OF KANSAS, LAWRENCE  
May 7, 1914

*Editor of the Journal of Industrial and Engineering Chemistry:*

Platinum valued at some six hundred dollars disappeared from one of the Chemistry Laboratories of the University of Minnesota sometime on Monday, April 27, 1914. This platinum consisted of eighteen crucibles—Nos. 20, 21, 22, 23, 26, 27, 29, 39, 40, 41 and 45 with covers of the same numbers and crucibles Nos. 35, 36, 37, 42, 44, 47 and 52 without covers; also one platinum dish that weighed about 43 grams.

If your readers hear of any platinum being offered for sale or have had any experience in the recovery of such property that might help us, we shall appreciate their immediate cooperation.

J. C. POUCHER

UNIVERSITY OF MINNESOTA, MINNEAPOLIS  
May 5, 1914

## PERSONAL NOTES

Dr. J. A. Watkin, of the U. S. Public Health Service, has been sent to Pittsburgh by the Secretary of the Treasury to investigate the effect of mill environment on the health of employees. This work, which constitutes a governmental innovation, will last until the end of the year.

Dr. Francis H. Eckhardt, research chemist for the Grasselli Company, died at the age of 46 on April 3rd at his home in Elizabeth, N. J.

Thomas H. Johnson, consulting engineer to the Pennsylvania Lines West, died in Pittsburgh on April 16th.

Prof. C. F. Chandler was the guest of honor at the 7th annual Dinner of the Columbia University Alumni Club of Philadelphia, April 17th, at the Hotel Adelphia. The speakers were

Professor Chandler, C. H. Mapes, Lemuel Whitaker, Robt. Arrowsmith, G. B. Compton and Arthur H. Elliot.

Prof. Alan W. C. Menzies, now head of the Department of Chemistry at Oberlin College, has been elected Professor of Chemistry at Princeton University.

Data collected recently by the College of Engineering of the University of Illinois show that of the 2,165 graduates, 1,933, or 89 per cent, are engaged in engineering work and that only 173 or about 8 per cent have gone into other fields.

Mr. H. de B. Parsons, of the Metropolitan Sewerage Commission, gave an illustrated talk on the plans as proposed by the Commission before the American Society of Mechanical Engineers, New York, May 12, 1914.

Among the members of the National Academy of Sciences elected at the annual meeting on April 23rd were the following: Moses Gomberg, University of Michigan; Edward Curtis Franklin, Stanford University; Francis Gano Benedict, Carnegie Institution.

Dr. Chas. L. Parsons spoke on "The Radium Work of the Bureau of Mines" before the North Carolina Section of the A. C. S., May 1st.

Messrs. Carnahan, Ahlbrandt and Aupperle, of the American Rolling Mills Co., addressed the Columbus Section of the A. C. S., May 8th, on "The Manufacture and Properties of Pure Iron."

The establishment of the Isaac Plaut Fellowship, the first traveling pharmaceutical fellowship in this country, was announced at a recent meeting of the Board of Trustees of the College of Pharmacy, Columbia University. The fellowship has been founded by Vice-President Albert Plaut, in memory of his father, for the encouragement of graduate study and original research. The fellow is to be selected from the graduating class in the College of Pharmacy and is to spend one year in study at a foreign university.

The trustees of Clemson College have appropriated \$300 for an investigation of the limestone and marl deposits of South Carolina and their value for agricultural purposes. The work will be in charge of Dr. F. H. H. Calhoun, Professor of Geology and Mineralogy.

The Southern California Section of the A. C. S. was addressed on May 21st by Dr. Chas. P. Lipman on "The Effect of Smelter Wastes on Plant Growth."

The program of the Kansas City Section of the A. C. S., on May 16th, included the following: "The Rare Earths and Their Separation," Dr. D. L. Randall, Baker University; "Recent Progress in Organic Industrial Chemistry," Mr. J. B. Whelan, University of Kansas.

The Forest Products Laboratories of Canada were established in the spring of 1913 under the Forestry Branch of the Department of the Interior and located on the grounds of McGill University at Montreal. The laboratories are to be modeled somewhat after those at Madison, Wisconsin, and are designed to study the best methods of utilizing the various native woods. Mr. John S. Bates, formerly with the Arthur D. Little, Inc., of Boston, was appointed Superintendent of the Laboratories on April 1st. Mr. Bates is also in direct charge of the Division of Pulp and Paper, which is the most important in the organization. An experimental paper mill capable of handling products on a semi-commercial scale is being equipped. The Timber Testing Division is now fully organized for Mechanical Testing and the Timber Physics Division is being started. Departments of Wood Preservation, Wood Pathology, etc., will be organized later. The scientific investigations are intended to act as a stimulus to wood-using industries and the organization will also serve as a Bureau of Information on Forest Products in Canada.

The U. S. Department of Agriculture has established an office in the Bureau of Chemistry for the promotion of a closer and more cordial cooperation among the city, state and federal food and drug officials of the country in the enforcement of the food and drug laws. Mr. J. S. Abbott, for nearly seven years dairy and food commissioner of Texas, was appointed to this office and began active service on April 3, 1914.

Prof. William Campbell, of Columbia University, spoke before the Rochester Section of the A. C. S. on April 6th, the subject being, "Some Uses of Metallography as a Method of Testing Materials."

The Louisiana Section of the A. C. S. was addressed at its 77th meeting, May 15th, by Mr. Chas. S. Williamson, on "Factors Influencing Soil Fertility—Some Modern Developments."

The following poem was written and read by Dr. P. N. Evans, of Purdue University, before the Indiana Section of the American Chemical Society at their annual banquet in February:

#### THE SENTIMENTAL SCIENCE

The public has a notion that our science is a thing  
That lodges in our brain-cells, but never makes us sing;  
That sentiment originates and grows within the heart,  
And never touches science, but inspires only art.  
It seems to me, however, that the case is not so bad—  
That science suffers only from the treatment that it's had  
From dry-as-dust professors, who can resist but not the lines,  
But see in every rose bush but an aggregate of spines.  
Who think they're scientific when they're burrowing in facts,  
And find no time for thoughts they're so submerged in streams of acts,  
And mercenary analysts, and office-holders too,  
And engineers, and routine hacks—of course I don't mean you,  
But unromantic people that refuse to see the thing  
That's right beneath their very nose—it makes me mad, by Jing!

Now chemistry is crowded with the tenderness of things—  
Attractions and affinities—of such it fairly sings;  
Its full of symbolism, fire, and feuds of families,  
And its most important element, you'll admit it surely is  
What poets in their frenzy vaguely feel but scarcely know,  
And gress by shouting madly in the strains of sentiment.  
The perfume of the flowers, too, is scarce so pure and sweet  
As our synthetic tribute is, with which it must compete;  
And nature's rainbow's so outclassed it's very rarely seen,  
It knows it could not stand the test of meeting aniline.

In asking of some Christian friends why steadfastly they cling  
To ritual, and formula, and symbol for a thing,  
They answer with sincerity, on higher things intent,  
The symbols and the formulas are but the sentiment.  
If formulas and symbols sentimental are, you bet  
Our chemistry's the most so of all things discovered yet!

And if in doubt you still remain, but turn your thought with me  
To names that throng organic books, and then I think you'll see  
That ester, yes, and ethylene, and ethyl, sit in state  
With cis and anti, polymer, and even silicate.  
And don't forget the sweetness in the carbohydrates show—  
The sweetest thing on earth is but a chemical, you know.  
The poets praise the ether, and they seem to think it's blue,  
But ethyl and O-ethyl is what it is—that's true.  
And then how like us humans do these little atoms act,  
With their strong and weak affinities—it certainly's a fact  
That the atom hates to live alone, but evidently yearns  
To establish some co-partnership, but from like atom turns  
To one of nature opposite, and when I grieve to state  
This kind of thing has happened very often of late,  
Though linked by well-established bonds, one of the pair perceives  
A fairer atom hovering round, it simply ups and leaves,  
And doubtless tells enquiring friends of cruelty and fights,  
And how a woman-atom now would boldly claim her rights.  
I hesitate to name a case, especially a pair  
Of which I formed one member and the other was so fair,  
But recently, I must admit, with Ethyl I had joined,  
Along came Sodium Ethylate—my better half purloined;  
Then Ethyl got—O Ethyl—and when I was bereft,  
I said "I'll take the Sodium that faithless thing has left."  
And Ethyl said I was the other who tried to break away,  
Each blamed it on the other, but who can really say?  
I didn't like that Sodium, and he didn't like to release,  
And then existed all alone—a period of peace;  
Then sought the aid of alcohol and phosphorus, and tried  
And found again my Ethyl! Now we're Ethyl Iodide.

This frequent change of partners is less likely to occur  
With solid folk who stay at home—he stays at home with her;  
In liquid state the restlessness increases very fast,  
And bonding grows less stable, and often does not last;  
But worst of all the cases that you or I have met,  
Are the volatile, unstable, vap'rous things, the dancing set;  
They whirl and dip, collide and bounce, and their velocity  
Increases with the temperature—the results we may foresee;  
From one step comes another, they hesitate, prove false,  
Then pivot, use the grape-vine—O this hesitation waltz!

We may well view with deep concern those substances that act  
Toward others in such a different mood it's sometimes worse than tact;  
Approached by some they seem to show their principles are such  
That we may safely count on them with others, just as much,  
To show the self-same nature, but we presently find out!  
From noting their behavior we're entirely in doubt  
What fundamental principles their conduct underlie—  
We call them tautomer, for of stronger terms we're shy;  
We might have called them double-faced, or hypocrites, or crooks,  
These tautomer substances of scientific books.

To prove again that sentiment is not to art confined  
Let me recount an incident that now I have in mind;  
It shows, I think, how different a thing may seem to be,  
How its effect is opposite, let's say, on A and B.  
The inference is obvious, that sentiment's the cause,  
So sentiment must be a part of laboratory laws.  
I have some water in the lab, quite normal every way;  
Its freezing point and boiling point were never known to stray;  
Yet freezing point and boiling point have proved themselves at fault  
And acted up quite contrary, because I added salts;  
The boiling point jumped up at once, in no way was distressed,  
Contrariwise, the freezing point was very much depressed.

I think I have convinced you that there's lots of sentiment  
In chemistry (and H<sub>2</sub>S is not the scent I meant);  
If I've omitted anything I hope you will forgive—  
You surely see the sentiment in that by which we live;  
It permeates our science just as light pervades the sky,  
And the chemistry of coal tar—it has taught us how to dye.



Dr. L. J. Henderson, Assistant Professor of Biological Chemistry, has been appointed the Professor from Harvard University for the second half of the year 1914-15 under the interchange agreement between Harvard University and the four Western colleges—Beloit, Grinnell, Knox and Colorado.

The Syracuse Section of the A. C. S. was addressed on April 24th by Mr. Carleton Ellis, of Montclair, N. J., on "Hydrogenation of Oils."

Mr. E. J. Sweetland, of the Sweetland Filter Press Company, New York City, sailed on May 19th for Europe, where he expects to spend some time on business.

Edward P. Hyde, Director of the Physical Laboratory of the National Electric Lamp Association, announces that hereafter the Laboratory will be known as the Nela Research Laboratory of the National Lamp Works of the General Electric Co., under which name its abstract-bulletin and other publications will appear.

Prof. George B. Frankforter, of the University of Minnesota, addressed the Detroit Chemists on "Some New Phases of Catalysis," April 24th.

Mr. Henry E. Jacoby announces the removal, on May 1st, of his offices to larger and more spacious quarters at 95 and 97 Liberty Street, New York City.

The Franklin Institute, Philadelphia, on May 20th, presented its Elliott Cresson Medals to Dr. Edgar Fahs Smith and Dr. Orville Wright. Addresses were made on "Scientists from the Keystone State," by Dr. Smith and on "Stability of Aeroplanes" by Dr. Wright.

Dr. Frank B. Kenrick, of the University of Toronto, gave an illustrated lecture on "Superheating and Supercooling" before the Rochester Section of the A. C. S., May 4th.

The Buffalo Foundry and Machine Company announce that they have withdrawn their New York representative and will handle all future inquiries in connection with their product directly through their Buffalo office.

The St. Louis Section of the A. C. S. was addressed by Prof. W. D. Harkins, of the University of Chicago, on "The Smelter Smoke Problem" at their meeting on May 11th.

Dr. Leo H. Baekeland, Charles Frederick Chandler Lecturer for 1914, has announced that the subject of his address, to be given at Columbia University on May 29th, will be "Some Aspects of Industrial Chemistry."

Smith, Emery & Co., Chemical Engineers and Chemists of San Francisco and Los Angeles, announce that Mr. Carlton R. Rose, for a number of years Superintendent of the U. S. Zinc Co., Pueblo, Col., subsidiary to The American Smelting & Refining Co., has recently resigned his position and become associated with them. Mr. Rose will be located in San Francisco.

Noel Deerr has resigned his position as director of the Experiment Station of the Hawaiian Sugar Planters Association to accept the appointment as Expert in Sugar Cane Agriculture and Sugar Manufacture to the Cuban Government.

Dr. Douglas McIntosh, Associate Professor in McGill University, Montreal, has been appointed Associate Professor of Chemistry and acting head of the Department in the newly established University of British Columbia.

## GOVERNMENT PUBLICATIONS

By R. S. MCBRIDE, Bureau of Standards, Washington

**NOTICE**—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate. Consular Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington. The regular subscription rate for these Consular Reports mailed daily is \$2.50 per year, payable in advance, to the Superintendent of Documents.

### TREASURY DEPARTMENT

**Treasury Decisions.** A weekly publication is issued giving the decisions of the board of general appraisers and the court of customs appeals in matters of duties on imports. Many of these decisions are of importance as showing the accepted classification of raw materials or manufactured articles of use in or in competition with American chemical industries. It is impracticable to review these decisions, and the original reports must therefore be consulted. The subscription price is \$1.75 per year, payable in advance to the Superintendent of Documents, Government Printing Office, Washington.

**Value of Foreign Coins.** Treasury Decisions, p. 6, No. 15, Vol. 26, dated April 9. Estimated by the Director of the Mint and adopted by the Treasury Department. Of industrial interest in foreign shipments, and especially in connection with imports.

### AGRICULTURAL DEPARTMENT

**The Effect of Heat on Hawaiian Soils.** By W. P. KELLEY and Wm. McGEORGE. Bulletin 30, Hawaii Agricultural Experiment Station. 38 pp. 10c. The results of the various physical and chemical changes produced in soils by heat are reported (see THIS JOURNAL, 6, 223).

**Rice Soils of Hawaii; their Fertilization and Management.** By W. P. KELLEY. Bulletin 31, Hawaii Agricultural Experi-

ment Station. 23 pp. 5c. Of interest in soil investigations for other tropical or semitropical regions.

**Service and Regulatory Announcements.** These monthly circulars issued by certain Bureaus give information, instructions, and notices of a regulatory nature. They are issued by the following Bureaus: Animal Industry, Biological Survey, and Chemistry, and the Insecticide and Fungicide Board.

**The Action of Manganese in Soils.** By J. J. SKINNER and M. X. SULLIVAN, assisted by others. Department Bulletin 42, from Bureau of Soils. 32 pp. 5c. The results given in this bulletin throw considerable light on the effect of catalytic fertility in various soils. Manganese as a fertilizer is practically unknown and untried in this country, so that discussion of its action is necessarily theoretical; yet it is of great interest to those growers whose technical training induces them to experiment with new substances to increase or control crop production.

**Laboratory and Field Assay of Arsenical Dipping Fluids.** By R. M. CHAPIN. Department Bulletin 76, from Bureau of Animal Industry. 17 pp. 5c. A popular account of laboratory tests for actual arsenious oxid and for total arsenic, together with methods of field assay for dips used for tick eradication. Of special interest to officials and others concerned with the analysis and control of these preparations.

**The Cost of Pasteurizing Milk and Cream.** By J. T. BOWEN. Department Bulletin 85, from Bureau of Animal Industry. 12 pp. 5c. This bulletin deals with the question of costs from an engineering point of view; the bulletin is addressed to managers of creameries and designers of pasteurizing apparatus.

**Alum in Foods.** Department Bulletin 103. 7 pp. 5c. A contribution from the Referee Board of Consulting Scientific Experts, giving their findings as to the effects of the use of alum in food.

**The Organic Nitrogen of Hawaiian Soils.** By W. P. KELLEY and ALICE R. THOMPSON. Bulletin 33, Hawaii Agricultural Experiment Station. 22 pp. 5c.

**The Agricultural Outlook.** Farmers' Bulletin 590, from the Bureau of Statistics. 20 pp. Includes among other crop estimates, a report on the Louisiana sugar crop of 1913.

#### BUREAU OF MINES

**The Prevention of Waste of Oil and Gas from Flowing Wells in California.** By RALPH ARNOLD and V. R. GARFIAS. Technical Paper 42. 15 pp. A preliminary report on measures to prevent or remedy conditions leading to oil and gas waste, as well as measures for preventing the escape of artesian waters into oil or gas strata.

**Weathering of the Pittsburgh Coal Bed at the Experimental Mine near Bruceton, Pa.** By H. C. PORTER and A. C. FIELDNER. Technical Paper 35. 35 pp. 5c. A large number of tests are reported on samples of weathered coal and coal from the same mine unaffected by weathering. The character of the work is indicated by the following general conclusions: "The weathering effects are manifested in a lower content of carbon and hydrogen and higher content of oxygen in the coal substance, a correspondingly lower calorific value of the coal, the presence of a larger proportion of combined water in the coal substance, and a much diminished power of consuming oxygen from the air and of liberating methane. A rusty appearance on the surface of lumps is not necessarily an indication of any depreciation in the fuel value of the coal."

**The Inflammable Gases in Mine Air.** By G. A. BURRELL and F. M. SEIBERT. Technical Paper 39. 24 pp. 5c. "The authors present this study as showing that normal mine-air samples obtained from many mines in various parts of this country contain only methane as the combustible gas." In addition to experimental results, there are given some historical data; and a description of the methods of analysis is also included. The apparatus used has been described previously by the Bureau of Mines.

**Fires in Lake Superior Iron Mines.** By EDWIN HIGGINS. Technical Paper 59. 34 pp. Principally of interest in mining work, but a considerable number of ore analyses and a discussion of the spontaneous ignition of pyritic material, such as black slate, are included.

**Drilling Wells in Oklahoma by the Mud-laden Fluid Method.** By A. C. HEGGEM and J. A. POLLARD. Technical Paper 68. 28 pp. Of interest in petroleum and natural-gas industries, as showing means of preventing waste during the well drilling.

**Gases Found in Coal Mines.** By G. A. BURRELL and F. M. SEIBERT. Miners' Circular 14. 24 pp. A popular treatment of this subject.

#### BUREAU OF FISHERIES

**A New Method for the Determination of the Food Value of Proteins, with Application to *Cynoscion Regalis*.** By G. F. WHITE and ADRIAN THOMAS. Document 784, from Bulletin 32. 5 pp. "Sørensen's method for the determination of amino acids was applied to a study of the tryptic proteolysis of *Cynoscion regalis*. The results were regular and in accord with those obtained by the nitrous acid method for the analysis for amino nitrogen. A practical method for the determination of the food value of proteins has therefore been developed."

**Properties of Fish and Vegetable-Oil Mixtures.** By G. F. WHITE and ADRIAN THOMAS. Document 785, from Bulletin 32. 14 pp. The viscosity, density, index of refraction, saponification number, acid number, and iodine number of the following oils were measured: China-wood, dogfish liver, soya-bean, linseed, and mixtures of these.

**The Effect of Water-gas Tar on Oysters.** By P. H. MITCHELL. Document 786, from Bulletin 32. 6 pp. Report of a laboratory investigation from which the following conclusions, among others, are drawn: "These experiments show no noticeable effects of water-gas tar on oysters in constantly-renewed sea water. This is true in spite of the fact that large amounts of tar mixed with stagnant sea water, or small amounts injected

into oysters which are kept in stagnant water, do cause serious or fatal effects." \* \* \* "In stagnant water the organism can not be effectively washed out, and effects involving a loss of sensitiveness in the mantle result. That consumption of the dissolved oxygen in the stagnant water by tar may have some effect on oysters is a possibility."

**The Oxygen Requirements of Shellfish.** By P. H. MITCHELL. Document 787, from Bulletin 32. 14 pp. A report on a laboratory investigation in which the "oxygen requirements" and the "resistance to lack of oxygen" were studied on oysters, clams and quahogs.

**Fishery Products.** Statistical Bulletins are issued, usually several each month, on the quantities and values of fishery products; for example, the following four subjects are covered in those issued during March, 1914: Quantities and values of products landed at Boston and Gloucester, Mass., in 1913, (1) classified by fishing ground, (2) classified by months, (3) for Jan., 1914, and (4) for Feb., 1914.

#### BUREAU OF STANDARDS

Bulletin No. 3 of Volume 10, contains the following 5 articles of chemical interest:

(1) **Critical Ranges of A<sub>2</sub> and A<sub>3</sub> of Pure Iron.** By G. K. BURGESS and J. J. CROWE. Scientific Paper 213. 56 pp. There is given a critical, historical summary of the experimental investigations of the position of A<sub>2</sub> and A<sub>3</sub>, a brief mention of the theoretical aspects of the subject, and a report on tests made on several samples of pure iron which were studied by two methods over the range 500 to 1000°. A new method of testing has been devised since the earlier work was reported and tests are now reported on samples prepared recently. The methods of testing, as well as the results, are given in detail. Without exception, 130 curves show A<sub>2</sub> and A<sub>3</sub> as sharply defined and distinct critical ranges. Reduced to basis of zero rate of heating, the results are: A<sub>2</sub> = A<sub>c2</sub> ± Ar. = 7680 ± 0.05; A<sub>c3</sub> = 9090 ± 1; and Ar<sub>3</sub> = 898° ± 2.

(2) **Note on the Setting of a Mercury Surface to a Required Height.** By M. H. STILLMAN. Scientific Paper 214. 4 pp. The improvement is simply an artifice to enable detection of a smaller dimple in the Hg surface; it consists of a scale of alternate white and black lines each 0.5 mm. wide placed behind the pointer so that the images of the lines appear parallel when the pointer does not touch the mercury but are distorted when the smallest dimple is formed.

(3) **Micrometer Microscopes.** By A. W. GRAY. Scientific Paper 215. 16 pp. This article discusses some errors affecting micrometer microscopes and methods of determination of the corrections and their applications.

(4) **The Pentane Lamp as a Working Standard.** By E. C. CRITTENDEN and A. H. TAYLOR. Scientific Paper 216. 28 pp. A discussion of the standardization adjustment, and use of the pentane lamp as a photometric standard, including detailed operating directions and tables giving corrections to be applied to correct for the effect of atmospheric conditions. A large number of results obtained during the use of lamps at the Bureau of Standards for several years, are summarized in the article.

(5) **Comparison of the Silver and Iodine Voltameters and the Determination of the Value of the Faraday.** By G. W. VINAL and S. J. BATES. Scientific Paper 218. 26 pp. A report on the comparison made of the silver voltameters of the form previously used by the Bureau of Standards and the iodine form used by Washburn and Bates, giving the following results:

Ratio of silver to iodine .....	0.85017
Electrochemical equivalent of iodine ..	1.31802
Value of the faraday (I = 126.92) .....	96,515
Value of the faraday (Ag = 107.88) .....	96,494
Value recommended for general use .....	96,500

**Industrial Gas Calorimetry.** By C. W. WADNER and E. F. MUELLER. Technologic Paper 36. (In press.) This paper reports an investigation of the factors which affect the accuracy

of the determination of heating value of gas, such as: Completeness of combustion, accuracy of the temperature measurements, the magnitude of the various heat losses from the calorimeter, the effect of varying the volume of the products of combustion, and the measurement of the quantities of gas and water. The summarized results are given of a critical study of 8 calorimeters of the flow type and one of the comparison type. There are also included the results of an experimental investigation of laboratory gas meters, showing the errors to which such meters are liable, the precautions to be observed, and the accuracy attainable in their use.

**Variations in Results of Sieving with Standard Cement Sieves.** By R. J. WIG and J. C. PEARSON. Technologic Paper 29. 16 pp. A report of tests made to determine the differences in standard sieves, the magnitude of the personal factor of the observer, the precision of results obtainable, etc.

**Some Leadless Borosilicate Glazes Maturing at about 1100° C.** By E. T. MONTGOMERY. Technologic Paper 31. 22 pp. Details are given of an attempt to prepare glazes equally desirable to substitute for those containing lead. Previous work, indicating the causes for the failure in this line, is confirmed.

**Production of Temperature Uniformity in an Electric Furnace.** By A. W. GRAY. Scientific Paper 219. 21 pp. A furnace giving the desired uniformity for work on the expansivity of metals is described.

**Standard Density and Volumetric Tables.** Circular 19, 4th edition, with supplement. The following tables (among numerous others of somewhat similar character) are given: Density of water; density of alcohol-water mixtures; temperature corrections for alcoholometers; density of methyl alcohol-water mixtures; densities of solutions of cane sugar and of sulfuric acid; temperature corrections for saccharometer readings; conversion tables for Baumé degrees, density, and specific gravity; density of air; apparent weight of water in air; temperature corrections for glass volumetric apparatus; and master scales for hydrometers.

**Polarimetry.** Circular 44. 140 pp. A very full report intended as a circular of information on the apparatus and methods of polarimetry, including a discussion of the theory involved, descriptions of the apparatus, its calibration, precautions to be observed in operation, and other methods. The circular is practically a text book of sugar methods as well as a laboratory handbook for general polarimetry. There are also included the U. S. Treasury Department "*Regulations Governing the Weighing, Taring, Sampling, Classification, and Polarization of Imported Sugars and Molasses.*"

**The Testing of Materials.** Circular 45. 90 pp. This circular is designed to give information on the subject of the testing done by the Bureau of Standards on each class of materials, the conditions under which such work is undertaken, and the limitation of such work due to the present status of technical knowledge. The information given is not only of interest in connection with the work done by the Bureau, since many of the topics are treated in such a way as to indicate the value and significance of tests, either chemical or physical, which can be made on certain sorts of materials.

#### BUREAU OF FOREIGN AND DOMESTIC COMMERCE

**Imports and Exports.** Several sets of publications are issued periodically by this Bureau, as follows:

(1) Exports of domestic breadstuffs, cottonseed oil, food animals, meat, dairy products, cotton, and mineral oils. This is a monthly bulletin, the number for February being No. 8 of the series 1913-14.

(2) Imported merchandise entered for consumption in the U. S., etc. This is a quarterly, subscription price 75c per year.

(3) Total values of imports and exports of U. S. A monthly series of pamphlets on this subject is issued.

(4) Monthly summary of commerce and finance of U. S.

This includes a section showing details of imports and exports, which section is sold in the form of advance sheets at 10c a single copy or \$1.00 per year.

**Trade Directory of South America.** Miscellaneous series publication No. 13 (1914). A report designed to promote American export trade with South America. Cloth, \$1.00.

**Production and Use of Denatured Alcohol in Principal Countries.** By CHAS. A. CRAMPTON. Special Agents Series 77. 32 pp. Paper 5c.

#### CONSULAR REPORTS, MARCH (Concluded)

The Potash shipments authorized for 1914 by the German Potash Syndicate amount to 635,300 tons of  $K_2O$  for domestic consumption and 531,300 tons of  $K_2O$  for foreign consumption. (P. 909.)

Public sales of Billiton Tin, in Batavia, in 1913, aggregated 4,938,800 lbs., at an average of \$0.4261 per lb. (P. 921.)

Russian Coal and Iron statistics show that the Donetz Basin provides 55.5 per cent of the coal consumed in Russia. The iron and steel industry shows increased activity. (P. 942.)

A large amount of Coconut Fiber (or Coir) is now wasted in Jamaica and the Philippines, but could be extracted and used for the manufacture of mats, etc., which are now made mostly from the British East Indian product. (P. 943.)

Coating of Coffees in Germany is regulated by law, especially the use of shellac, etc., which may contain arsenic. (P. 954.)

Wood Block Pavements in Berlin are made of blocks impregnated with zinc chloride or creosote, and laid in tar or asphalt, on a concrete base. (P. 956.)

The Commercial Museum of Trieste, maintained by the Chamber of Commerce, furnishes commercial and tariff information, investigates industries, and examines and analyzes imported goods. (P. 958.)

An exposition of machinery, apparatus, and supplies used in Wine Production, Brewing and Distilling, will be held in Budapest, May 23, to July 6, 1914. (P. 971.)

Spanish Garnets from Almeria Province are imported into the U. S. for abrasive purposes. (P. 974.)

A commercial review of Nova Scotia Ports includes statistics of the Coal and Iron Industries of that region. (P. 977.)

As a result of Rubber Cultivation in Choco, Columbia, 1,500,000 trees have been planted. Alluvial deposits of Gold and Platinum in Choco are being worked, mostly by hand. (P. 997.)

Petroleum production in Burma in 1912 amounted to 240,500,000 gallons. (P. 1007.)

The Sugar Crop of Austria-Hungary in 1912-13 showed a large increase in the production of beet sugar over previous years. (P. 1031.)

The Constantinople Gas Works has been purchased by a European firm, who will sell gas at \$1.43 per 1000 cu. ft. for lighting, \$1.14 for cooking, and \$1.00 for power. (P. 1051.)

Rubber shipments from the Amazon Valley in January, 1914, were lower by 2,877,799 lbs. than in January, 1913. (P. 1055.)

The United States supplied 65 per cent of the Coal imported into Ecuador in 1913. (P. 1063.)

All the Oil and Gasoline used in Prince Edward Island, Canada, is imported from the U. S. (P. 1070.)

The output of Vegetable Butter and Oils, principally from cocoanut oil, in Odessa, has increased rapidly in the last few years. (P. 1071.)

The Olive Oil production of Tuscany for 1913-14 was only one-third the normal output. (P. 1083.)

Petroleum in Persia is being exploited by three companies. (P. 1083.)

The cultivation of Sugar-cane has largely supplanted the Wine industry of Madeira. (P. 1095.)

The Governments of British Columbia and Ontario have passed regulations regarding the development of Radium deposits and have offered rewards of \$5,000 and \$25,000, respec-



tively, to persons discovering workable radium deposits in these provinces. (P. 1110.)

The statistics of the Russian sales to the U. S. for 1912 and 1913 include **Chemicals, Fertilizers, Glue, Sheet Iron, Manganese Ore, Fusel Oil, Mineral Oil, Platinum, Rubber, Liquors, Tar, Turpentine, and Wood Pulp.** (P. 1112.)

**Petroleum** is being prospected for in Palestine. (P. 1115.)

A new **Glass Factory** at Tobata, Japan, to cost \$1,000,000, is nearly completed and will make sheet and plate glass. (P. 1125.)

**Platinum products** manufactured in Switzerland may be officially stamped to indicate the platinum content (iridium being considered as platinum). (P. 1128.)

Exports of **Tin** from Hongkong to the U. S. in 1913 showed an increase while the exports to Europe showed a marked decrease. (P. 1148.)

The Antwerp **Diamond** trade flourished in 1913, Antwerp being now ahead of Amsterdam in this industry. The International **Metric Carat** of 200 milligrams has now been adopted by Belgium and the U. S., leaving England as the only important country in which it has not been adopted. (P. 1169.)

**Cocoa Beans** in Trinidad are usually coated with clay to preserve them and render them uniform in color. Efforts are now being made to prevent fraudulent excessive claying. (P. 1176.)

South African Collieries produced 4,500,000 tons of **Coal** in 1913, so that only 65,000 tons were imported from Great Britain. (P. 1177.)

The trade statistics for Ceylon for 1912 and 1913 include in the exports **Cocoonut Fiber and Oil, Citronella Oil, Plumbago, and Rubber.** Imports include **Cement, Coal, Iron, Fertilizers, Kerosene, Sugar and Lead.** (P. 1185.)

**Vinegar and Pyroligneous acid** are admitted free to the Netherlands when intended for use in **Zinc Etching Establishments.** (P. 1203.)

In connection with the reduction of the duty on **Sugar, Syrups, etc.,** into Sweden, syrups are defined as containing not over 70 per cent sugar and more than 1.3 per cent ash. (P. 1205.)

#### CONSULAR REPORTS, APRIL

According to a bulletin of the Philippine Bureau of Agriculture the **fiber** or floss from the fruit of the **kapok** tree is being used extensively for filling mattresses, life-saving appliances, etc.; it can also be spun into yarn. (P. 10.)

Statistics of the **zinc industry** show that the world's production of zinc in 1913 was the largest ever recorded. Separate statistics are given for Australia, Austria Hungary, Germany, Italy, Russia and Spain. (P. 17.)

The **beet sugar industry** in Canada is conducted in 3 factories, the output of which in 1913 was 27,232,124 lbs. raw sugar. (P. 30.)

Statistics of the **iron and steel** production and the iron reserves, reported by the British Board of Trade, show the consumption of iron ore and the production of pig iron and steel for the principal countries, in 1910, 11 and 12. The deposits of ore now being worked will supply the world for less than two centuries, but known deposits as yet unworked, will greatly increase the supply. (P. 40.)

**Pyrite** deposits in Norway, containing 33 per cent sulfur, and 1 per cent copper are about to be worked on a large scale, the proposed annual output being 100,000 tons. (P. 43.)

The important mineral products of Nova Scotia are **coal, gypsum, and limestone.** (P. 43.)

The principal mineral products of China, are **coal, iron, copper, tin and antimony.** (P. 45.)

A trade review of Liverpool includes figures for the trade with U. S. in **metals, drugs, oils, rubber, etc.** (P. 49.)

The British Navy has just made large contracts for **Scotch shale oil**, for fuel. (P. 78.)

The foreign commerce of the Philippines in 1913 includes exports of **copra, hemp, and sugar.** (P. 92.)

The Scotch mineral oil companies produced 75,000,000 gallons of oil in 1913. Illuminating oil sold for \$0.14 per gal., and "motor spirit" for \$0.30 per gal. (P. 101.)

The principal minerals obtained in the Madrid district in Spain are **coal and iron.** (P. 134.)

The **lime-fruit** industry of Dominica in the Seeward Island includes the manufacture of **calcium citrate** and oil of limes. (P. 142.)

A great increase in the imports of **fertilizers** into Japan is noted. (P. 143.)

Both imports and exports of the Japanese foreign trade showed a marked increase in 1913. The imports included **dyes, fibers, rubber, iron, fertilizers, paper pulp, and sugar.** The exports included **coal, copper, whale oil, menthol, and camphor.** (P. 148.)

The production of **maple syrup** and **maple sugar** in the U. S. and Canada is rapidly decreasing. (P. 150.)

Methods of **detinning** in Germany include electrolytic methods, using both alkaline and acid electrolytes, and the chlorine method, the latter being most used. (P. 151.)

Cardiff, Wales, is the world's principal coal shipping port. **Iron and steel, tin plate and galvanized steel** are produced there in large amounts. Total shipments of coal from ports in Wales in 1913 were 40,000,000 tons. (P. 161.)

A new **oil-bearing nut** has been discovered in the Philippines belonging to the family Meliaceae. The dry nuts yield 45 per cent of oil which produces a good grade of soap. The production of **cocoonut oil** in the Philippines has increased very rapidly. (P. 172.)

The mineral products of Somerset, England, include **coal, lead and zinc ores, fire clay, fuller's earth, and celestite** (strontium sulfate). Imports of **petroleum oils** into Bristol are increasing. Large amounts of **oil-seeds** are imported for the manufacture of **vegetable oils**, including cottonseed, linseed, and soya bean. (P. 177.)

**Fertilizers** are to be admitted free of duty to all Belgian colonies after Jan., 1914. (P. 209.)

At a conference of commercial gas users in London, England, it was stated that municipal gas plants do not sell as large quantities of gas per consumer as do private companies. The increased use of **gas stoves** in London has materially improved the fog conditions. (P. 220.)

**Italian olive oil** is frequently adulterated with treated olive oil, *i. e.*, oil that has been deodorized or decolorized by chemical means and the presence of which is very difficult to detect. (P. 222.)

Exports from Manitoba, Canada, include **flaxseed, wood pulp, and pyrite.** (P. 232.)

Linseed and sunflower seed are used extensively in Russia for the production of **vegetable oils.** (P. 242.)

In the Spanish **olive-oil** industry the oil from the first two pressings is sold for edible oil, and that obtained by extraction with carbon bisulfide is used for industrial purposes. Inferior oils, when deodorized and decolorized are sometimes mixed with high-grade oil. To prevent adulteration of olive oil with other oils, the law requires the addition of wood pitch or coal tar to any **cottonseed or rapeseed oil** imported. (P. 246.)

In the manufacture of **sawdust briquettes** in British Columbia, the sawdust, chips, etc., are sometimes compressed into briquettes without the use of a binder, though usually coal dust and tar are added. (P. 249.)

Exports from Haiti to the U. S. include **beeswax, cottonseed, lignum-vitae wood and gum, logwood, and fustic.** (P. 266.)

**Refrigeration** in France is increasing in storage houses, cars and vessels. In cars, small machines, using  $\text{CH}_2\text{Cl}$  and operated by power from the car wheels, are frequently used. (P. 269.)

Exports from Belgian Kongo include **copal, gum, copper, gold, palm nuts and oil, mabula panza** (an oil nut) and **rubber**. (P. 273.)

The production of **petroleum** in the Dutch East Indies in 1913 was over 1,500,000 tons. (P. 285.)

Exports from Persia include **drugs, gums, genna** (a vegetable pigment), **hides, and precious stones**. (P. 298.)

The campaign for **smoke abatement** in England includes accurate measurement of atmospheric pollution in all the large cities, organization of classes for engineers and stokers, and the use of various forms of smoke-preventing apparatus. (P. 301.)

An increase is noted in the export from Ceylon of **papain**, a digestive extract from the Carica papaya. (P. 302.)

The export of **peanuts** from Hongkong to the U. S. has increased. (P. 311.)

The exports of Australia include **coal, copper, chemicals, gold, lead, fertilizers, silver, soap, tallow, and tin**. (P. 321.)

The exports of Trinidad include **asphalt, balata gum, copra, petroleum, sugar, and molasses**.

In the wine industry of Argentina, the grape residues are distilled for **alcohol**, and some **tartaric acid** and **cream of tartar** are recovered. (P. 335.)

Owing to adulteration of Chinese **cassia** (cinnamon) with dirt, sticks, etc., new standard contracts have been made. Large amounts of the spice and the oil are imported into the U. S. (P. 348.)

A company has been organized to develop **nickel and iron** deposits in Athabaska, Canada. (P. 349.)

Exports from Curacao (Dutch West Indies) include **coal, dividivi, hides, salt, gold, phosphates, and aloes**. (P. 358.)

The exports of New South Wales include **coal, copper, gold, lead, leather, hides, cocoanut oil, silver, tallow, and tin**. (P. 401.)

Exports from Manchuria include **soya bean, cake and oil, coal, hemp, ginseng, and castor oil**. (P. 417.)

The **aluminum** industry in the United States yielded dividends of 20 per cent in 1913. (P. 425.)

Importations of crude **petroleum** oil and kerosene into Hongkong from the U. S. showed a marked increase in 1913. (P. 436.)

**Soya beans** from Southern Manchuria contain 16-17 per cent of oil, and those from Northern Manchuria only 15 per cent of oil. (P. 439.)

Importations of chemical **fertilizers** into the Canary Islands are increasing. (P. 443.)

Imitation **gold leaf**, "blatt-metall," consisting of 100 parts copper and 15-20 parts zinc, is made and used extensively in Germany. Imitation **silver leaf** consists of 90 per cent tin and 10 per cent zinc. (P. 446.)

The first **natural gas** pipe line in Hungary was recently completed. (P. 451.)

Exports from Lombardy to U. S. in 1913 included **drugs, dyeing and tanning extracts, glycerine, glue, and "oleostearin"**. (P. 455.)

A thorough investigation has shown that Southern India is well adapted to the cultivation of **sisal hemp**. (P. 461.)

The new Canadian tariff includes changes in the rates of duty on **iron and steel, amyl alcohol, peanut and soya-bean oils, chloride of lime, and caustic soda**. (P. 482.)

Exports from Paris to the U. S. include **aluminum, glue, glycerine, marble, platinum, iridium, palladium, rubber, silver, and wines**. (P. 519.)

Exports from Hongkong to the U. S. include **aniseed oil, camphor, cassia, cassia oil, peanuts, peanut oil, sugar and tin**. (P. 529.)

A prosperous industry in Turkestan is the cultivation of **Sevant** wormseed, from which the drug **santonin** is extracted. (P. 539.)

Exports from Almeria, Spain, include **iron, zinc, lead, and copper ores and garnets**. (P. 553.)

A plant has been erected in British Columbia to use the Laurentia process for pasteurizing milk, in which the milk, after having been heated to 155-165° F., is passed through a "homogenizer" in which the fat globules are broken up. (P. 557.)

Exports from Glasgow to the U. S. include **aluminum, ammonium, and potassium salts, creosote oil, and iron**. (P. 574.)

A Florentine inventor, Ulivi, claims to be able not only to **explode powder**, etc., by the so-called "**F rays**," but also to locate mineral deposits. (P. 587.)

## BOOK REVIEWS

**Allen's Commercial Organic Analysis.** Vol. VIII. Edited by W. A. DAVIS AND SAMUEL S. SADTLER. 4th edition, 696 pages. Philadelphia: P. Blakiston's Son & Co., 1913. Price, \$5.00 net.

This is the last volume of the fourth edition of a work which has been long and favorably known, and which has become a practical necessity in laboratories where technical investigations in any field of organic chemistry are carried out. The present volume deals with the protein and related substances, or those products in which the proteins are the most characteristic or important elements.

The revision of a work of this character has long passed beyond the power of a single individual because no one person can be expected to be expert in so many specialties. In this volume, as in the others of the series, we find the labor has been divided among a number of men, in this case eleven, all of whom are well known authorities in different fields of technical chemical research. The general editorship remains with Messrs. Davis and Sadtler. The contributors to the various sections of Volume VIII are E. Frankland Armstrong, S. B. Schryver, L. L. Van Slyke, Henry Leffmann, Cecil Revis, E. Richards Bolton, W. D. Richardson, J. A. Gardner, G. A. Buckmaster, Jerome Alexander and W. P. Dreaper.

In the last edition of the work, the volume which covered the same general ground was issued about fifteen years ago. Since then there have been great advances in all lines of technical organic chemistry, and especially in our knowledge of the protein substances and related bodies which are taken up here. These changes have been so great as to call practically for the rewriting of the whole book. In general, the work has been well done and apparently the most recent literature has been considered in every field covered.

The longest single section is that by W. D. Richardson on Meat and Meat Products. This covers 205 pages, or nearly one-third of the whole book. Mr. Richardson, as head of the laboratory of one of the largest meat-producing plants in the world, has had opportunities such as are open to but few men for becoming acquainted with the whole field described and this is shown by the wealth of first-hand information evident in every part of the text, in the discussion of analytical methods as well as in the presentation of details of production.

The large field of Proteins of Milk, Milk and Milk Products has been covered by L. L. Van Slyke, H. Leffmann, and Cecil Revis and E. R. Bolton in chapters filling 147 pages. Each one of the authors has long been known as an original investigator in the subject of the chemistry of milk. There are few fields

in which methods of analysis have been so abundantly supplied as in that of milk investigation. In reading these sections one is impressed by the fact that little of importance is omitted. The discussion of the various products formed from milk is excellent. (Butter is considered in another volume.) It is interesting to note that the much advertised Sanatogen is described as a mixture of casein and sodium glycerophosphate, or possibly as a salt of casein so mixed.

Somewhat shorter sections have been contributed on Enzymes and on Proteins of Plants by E. F. Armstrong; on Proteins and Albuminoid Substances, and on the Digestion Products of the Proteins by S. B. Schryver, on Hemoglobin and Its Derivatives by J. A. Gardner and G. A. Buckmaster; on Albuminoids or Scleroproteins by Jerome Alexander; and on Fibroids by W. P. Dreaper. It will be noticed that there is some confusion in the use of the term albuminoid. In the discussion of the digestion products of proteins, the description of Pancreatin does not correspond very well to what is actually produced in this country. Under the methods used in testing enzymic activity the author describes the convenient Fuld method for pepsin but does not describe the corresponding method, using casein, by the same authority, for trypsin. There appears to be no mention of the value of fibrin in the estimation of marked tryptic activity. The routine method of the British Pharmacopoeia for the examination of pepsin is given, but not the somewhat similar but more rapid method of the U. S. Pharmacopoeia. As the latter work is an official standard in this country the oversight should have been caught by the editors and corrected.

Attention must be called to the excellent chapter on hemoglobin, embracing the methods of blood examination for scientific or clinical work.

J. H. LONG

#### The Electric Furnace, Its Construction, Operation, and Uses.

By ALFRED STANSFIELD, D.Sc. McGraw-Hill Company, New York. 415 pages. \$4.00 net. 1914.

The present volume, which is the second edition, is just double the size of the first edition of 1907. In these seven years there have been great advances in the subject of which this book treats, and Dr. Stansfield has met this change in an admirable manner, and it is only fair to say that it is by far the best book which has thus far appeared on the electric furnace.

The first chapters deal with the history, classification and efficiency of electric furnaces. Good illustrations are here given of the different types of arc and resistance furnaces, with a short description of each. Under the efficiency of electric furnaces, data are included as to cost of power, etc., and the actual method of calculating the efficiency is illustrated by taking a typical run of a Héroult steel refining furnace.

Much valuable data are given under "Construction and Design," as to the properties of refractories, resistors, electrodes, etc., with a good summary of Hering's papers on heat losses in electric furnaces. In the operation of furnaces we find methods for the control and measurement of power, descriptions of transformers suitable for large operations, and diagrams of connection for furnaces using polyphase circuits.

Some interesting figures are given as to the power densities employed in various types of furnaces, and the extraordinary densities used by Moissan account for many of the remarkable results which he obtained.

The measurement of temperature and description of pyrometers is taken up very briefly, which is perhaps just as well as we already have the excellent book of Burgess which deals with this subject exclusively.

Under laboratory furnaces we find descriptions of Hutton's pressure, Arseny vacuum, Harker tube, and the Hansen arc furnaces among many others. The subject of iron and steel is given about 100 pages of the book, and the latest developments in

this important branch are well treated, all of the important furnaces being described.

The balance of the book is taken up with furnaces for the production of carbides, graphite, silicon, sodium, aluminium, nitric acid, zinc, alundum, etc., and well describes the improvements which have been brought about in their manufacture.

Calcium cyanamid is now produced in such enormous quantities that more should have been said about it, and it would have been well to have mentioned something as to the Serpek process or the fixation of nitrogen.

The book is unusually well illustrated and is an important and timely addition to the literature of the subject in which so many are now interested.

SAMUEL A. TUCKER

#### Principles and Practice of Agricultural Analysis. By HARVEY

W. WILEY, A.M., Ph.D. Volume III, *Agricultural Products*, pp. i-xv and 1-846. The Chemical Publishing Co., Easton, Pa. Price, \$6.00.

The appearance of the second edition of this truly remarkable volume has been delayed, as the author states in the preface, by stress of other duties which made it impossible for the author to bring it up to date. It is divided into seven parts, the first discussing methods of sampling and drying, the second and third being devoted to sugars, starches and carbohydrates, the fourth to fats and oils, the fifth to nitrogenous bodies, the sixth to dairy products, and the seventh to miscellaneous products under some twelve subheads. It is essential to everyone concerned with those branches of agricultural chemistry with which it specifically deals, not only for the information included in the pages, but as a guide to original articles, which, in most cases, the expert will wish to consult directly. The student of Agricultural Chemistry who wishes to learn more than the mere laboratory technique must also go to the original articles, for the theoretical basis of the formulas in many cases and the processes sometimes are discussed quite insufficiently. The expert who has specialized in particular lines will occasionally be disappointed. For instance, in describing the calcium saccharates (p. 274), there is no mention of Patten's research work [*Jour. Phys. Chem.*, 15, 67 (1911)]. The volume does not, however, pretend to quote the literature exhaustively, and it is amazing that so much has been included, especially of the American literature. As is natural, those methods which have been tested in the Bureau of Chemistry of the U. S. Department of Agriculture receive special consideration. This fact is, moreover, a very valuable feature of the volume. The wealth of formulas and tables make the book of extraordinary value for quick reference. A charming, as well as valuable, feature is the occasional introduction of historical matter, as in the discussion of Fehling's solution (p. 174, *et seq.*). There is a good index, and the general makeup of the volume is satisfying.

FRANK K. CAMERON

#### Metallography. By CECIL H. DESCH, D.Sc. (Lond.), Ph.D.

(Wurz.), Graham Young Lecturer in Metallurgical Chemistry in the University of Glasgow. \$3.00 net. Second edition. Longmans, Green & Co.

The second edition of this book incorporates some of the most important results of recent investigations and brings up to date the references to publications. There is no change in treatment of the subject.

The book is divided into eighteen chapters, which deal with the following headings: Introduction; The Diagram of Thermal Equilibrium; Solid Solutions or Mixed Crystals; Ternary and More Complex Systems; Metals which are only Partially Miscible in the Liquid State; Practical Pyrometry and Thermal Analysis; The Preparation of Micro-Sections; The Microscopical Examinations of Prepared Sections; The Crystallization of Metals and Alloys; Undercooling and the Metastable State; Diffusion in the Solid State; The Physical Properties of Alloys; Density—Thermal Expansibility—Hardness—Electrical Conductivity—



Thermo-Electric Power—Magnetic Properties; Electromotive Force and Corrosion; The Construction of the Equilibrium Diagram; The Molecular Condition of Metals in Alloys and the Nature of Inter-Metallic Compounds; The Plastic Deformation of Metals and Alloys; The Metallography of Iron and Steel; The Metallography of Industrial Alloys.

This book is one of the text books of Physical Chemistry edited by Sir William Ramsay, and naturally takes up the study of metallography from that point of view. It sets forth, very clearly, our present knowledge of this subject which has been defined as the study of the internal structure of metals and alloys and its relation to their composition and to their physical and mechanical properties. The author, in a very clear manner, works out the various diagrams of thermal equilibrium and then discusses the ternary systems. The section on practical pyrometry and thermal analysis gives us in some forty chapters a clear and concise account of the methods in use and instruments for autographic registration of curves. The chapter on the crystallization of metals and alloys is well written and well illustrated by micrographs. From the chapter on the physical properties of alloys we get a very clear idea of what has been done and what remains to be done in this branch of the subject. The section dealing with the metallography of iron and steel gives us a brief summary of our present knowledge of this subject. The system iron-carbon presents considerable difficulties: the most widely accepted hypothesis is that we have two systems, Austenite-Graphite or the stable, and Austenite-Cementite or the metastable. Goerens, however, is of the opinion that graphite is always the product of decomposition of cementite; Upton's diagram avoids many of the difficulties of the double diagram. Carpenter and Keeling's thermal observations show arrests at 800 and 600°, respectively. Under conditions of equilibrium the two solid phases separating from the liquid are Austenite and graphite; at 1095° they react to form Fe<sub>3</sub>C, at 800° this decomposes into Fe<sub>3</sub>C, at 615° a further decomposition occurs and Fe<sub>3</sub>C changes into Fe<sub>3</sub>C and alpha iron. These three carbides all resemble cementite, and means of distinguishing them have yet to be found. The book ends with an appendix consisting of tables of systems of which the equilibrium diagrams have been published. The book is to be recommended, first, because it covers the ground very thoroughly, and secondly, because the author speaks about what he is evidently thoroughly familiar with from the practical standpoint. It is not merely a compilation of the work of others. Although the field is a wide one, Dr. Desch has covered it well and the book will continue to be of great assistance to those starting out in metallography, not only for what it contains, but also as a guide to further work on the subject.

WILLIAM CAMPBELL

**Sugar Analysis:** For Cane-Sugar and Beet-Sugar Houses, Refineries and Experimental Stations and as a Handbook of Instruction in Schools of Chemical Technology. By FERDINAND G. WIECHMANN, Ph.D., Third Edition, 8vo. 303 pages. 7 Figures. Cloth, \$3.00 net.

In the present volume, Dr. Wiechmann—the dean of American sugar chemists—has given us the best results of his ripe and many-sided experience as teacher, refinery expert, consulting chemist and secretary of the International Commission for Uniform Methods of Sugar Analysis. Certainly no one is better qualified than he to discuss fully and adequately the many difficult phases which underlie the treatment of this subject.

As stated by the author in his preface the aim in preparing the present edition has been "to cast his material in a form in which it would prove most readily available in the several branches of the sugar industry." The purpose thus expressed has been most admirably fulfilled.

The scope of the new volume is briefly indicated by the following synopsis of chapters: I, Properties of Sucrose; II, Instruments Used in Sugar Laboratories (Refractometers, Balances,

Hydrometers, Colorimeters, etc.); III, Polariscopes and Accessories; IV, Sucrose Determination by Optical Analysis; V, Sucrose Determination by Chemical Analysis; VI, Sucrose Determination by Optical and Chemical Analysis; VII, Constituents of Sugar other than Sucrose (Reducing Sugars, Water, Ash, Suspended Impurities, Organic Non-Sugar, Nitrogenous Substances, Gums, Acids, Iron Oxide, etc.); VIII, Materials Used in the Sugar Industry (Bone-Black, Phosphoric Acid, Limestone, Coal, Flue Gases, Sulfur, Oils, Waters, etc.); IX, Analytical Control in Cane-Sugar Manufacture (Sugar Cane, Juices, Syrup, Bagasse, Press Cake, Sugar, Molasses, etc.); X, Analytical Control in Beet Sugar Manufacture (Beets, Diffusion Juices and Waters, Thick Juices, Fill Mass, Raw Sugars, Molasses, Cattle Food, etc.); XI, Analytical Control in Refineries; XII, Résumé of the Work of the International Commission for Uniform Methods of Sugar Analysis.

All sugar chemists who have occasion to consult the Proceedings of the International Commission will thank Dr. Wiechmann for the résumé in his 12th chapter which contains information that was formerly widely scattered and often difficultly accessible.

A well-selected list of sugar tables and an index make up the final 70 pages of the volume.

The typography and general appearance of the new book are excellent and leave nothing to be desired.

The many friends of the previous editions of Dr. Wiechmann's "Sugar Analysis" will welcome the new edition of this standard work. It is a most useful guide not only to the student, but also to the sugar factory chemist and commercial analyst.

C. A. BROWNE

**Industrial Poisoning from Fumes, Gases and Poisons of Manufacturing Processes.** By DR. J. RAMBOUSEK. Translated and edited by THOMAS H. LEGGE. New York: Longmans, Green and Co., 1913. xiv + 360 pages, with illustrations. Price, \$3.50, net.

Efficiency is the dominant idea in modern industry. Justice Hughes once said that we do not wish to see productive energy sapped by excessive toil or by labor under improper conditions; for, to quote Sir John Simon, "the canker of industrial diseases gnaws at the very root of our national strength." It is, therefore, only to be expected that various governments and scientific organizations are taking a growing interest in the diseases of occupation. Several countries have, for some time, been active in this field; there is now a Permanent International Committee for the Study of Industrial Diseases; and, in this country, the New York State Department of Labor, the American Museum of Safety, the Health-Education League of Boston, the Federal Bureau of Mines and the Museum of Natural History of New York have recently shown interest of purpose. The translation of Rambousek's treatise on the industries and processes attended with risk of poisoning, the incidence of such poisoning, the pathology and treatment of industrial poisoning, and the preventive measures against industrial poisoning, supplies English readers with a book wherein the whole subject of industrial poisoning is well discussed.

In his preface Rambousek states that "the book is intended for all who are, or are obliged to be, or ought to be, interested in industrial poisoning;" the translator and editor observes that no words could better describe the scope of the book, and it seems to the reviewer that the general subject matter is presented in as comprehensive and systematic a manner as is possible within the compass of a single volume of this size. Several omissions occur in the text: no reference is made to poisoning produced by vanadium ore and oxide, and the effects of osmium oxide vapor are not noted. On the whole, however, the book is very complete.

American investigators have much to learn from European reports on industrial diseases and factory hygiene, and it will be surprising to many to find how thorough are the regulations

for dangerous trades abroad. A wealth of references to the work of foreign writers occupies sixteen pages (unindexed, but chronologically classified under subjects), while the general index of the book is well done.

W. A. HAMOR

**The Nickel Industry: With Special Reference to the Sudbury Region, Ontario.** By A. P. COLEMAN, Ph.D. Published by the Department of Mines, Mines Branch, Ontario, Canada. *Bulletin* No. 170. Size, 6 1/2 by 10 inches. 189 pages of text, 8 pages of index, and 9 pages of the publications of the Mines Branch of Canada Department of Mines.

The author, in his letter of transmittal to the Director of the Mines Branch, Department of Mines, Ontario, Canada, states in part: "I have the honor to transmit to you a Monograph on the Nickel Industry, with special reference to the Sudbury region, with a general map, and special maps of the more important mines, the whole representing the advance made in our knowledge of the region due to three summers' work in the field. In addition to descriptions of all the known nickel ore deposits in Ontario, there are accounts of methods of mining and smelting the ores, and of the chief nickel regions of other countries."

The methods of mining and of smelting of the ores of Ontario are described, and also descriptions of proposed methods for the treatment of copper-nickel ores and of the separation of copper from nickel and from their alloys. The divisions are not handled with the idea of the importance of any one of the ranges, but in such a way that a connected treatment of the subject as a whole is given. This bulletin supplements Report No. 873 of the Geological Survey of Canada by A. E. Barlow, M.A., D.Sc., on "The Origin, Geological Relations and Composition of the Nickel and Copper Deposits of the Sudbury Mining District," which was published in 1904.

The first 19 pages are devoted to outlining the geology of the

Sudbury district and to an historical sketch of the leading mines. The next 95 pages contain a description of the ores, their mineral constituents, and the individual deposits of the more important mines. Mention is made as to the origin of the ore bodies, and the genesis of the minerals of which the typical ores are composed.

A section (pp. 116 to 125) is devoted to the better known nickel-producing districts of the United States, Europe, New Caledonia, and the Cape Colonies, for the purpose of comparison with the Canadian ranges.

Methods of prospecting and mining (pages 125 to 132) are given, and are accompanied by illustrations. The mechanical and metallurgical treatment of the nickel-copper ores is gone into thoroughly (pp. 132 to 167), starting with the ore from the time that it is hoisted from the mine and finishing with the purified copper and nickel, and the purified Monel metal. This part of the monograph is extensively illustrated by plate photographs and drawings of the processes used.

The appendix (pp. 171 to 189) contains copies of patents of methods of separating copper and nickel from ores and from alloys.

The monograph is profusely illustrated by 62 plate photographs, 14 drawings of the principal mine sections and of metallurgical flow-sheets and apparatus, and 8 geological maps of the principal ranges of the Sudbury district.

This monograph is a valuable addition to the literature on the mining of nickel ores and the metallurgy of nickel, and will be welcomed by the mining man, the metallurgist and the metallurgical chemist, for there is so little reliable literature on the subject. This, like all of the publications of the Canadian Government, is well gotten out, and one holds the assurance that the information is reliable.

E. F. KERN

## NEW PUBLICATIONS

By D. D. BEROLZHEIMER, Librarian The Chemists' Club, New York

**Alloys and Their Industrial Applications.** By EDWARD F. LAW. 2nd Ed. 8vo. Price, \$3.25. Chas. Griffin & Co., London.

**Arsenic, Antimony and Tin, Methods of Determination of, and Their Separation from the Other Elements.** By H. WOELBLING. L. 8vo. Price, \$3.75. Ferdinand Enke, Stuttgart. (German.)

**Carbides and Silicides.** By OTTO HORNIGSCHMID. 8vo. 265 pp. Price, \$4.75. Wilhelm Knapp, Halle. (German.)

**Carbohydrates, Short Handbook of.** By B. TOLLENS. 3rd Ed. 8vo. 816 pp. Price, \$5.25. J. A. Barth, Leipzig. (German.)

**Chemistry in America.** By EDGAR F. SMITH. 8vo. Price, \$2.50. D. Appleton & Co., New York.

**Chemistry, Some Fundamental Problems in Old and New.** By E. A. LETTIS. 8vo. 227 pp. Price, \$2.00. Constable & Co., London.

**Coal Tar Distillation.** By ARTHUR R. WARNES. 8vo. 185 pp. Price, \$2.50. D. Van Nostrand Co., New York.

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**Copper Handbook, Vol. XI.** By WALTER HARVEY WEED. 8vo. Price, \$5.00. Walter Harvey Weed, Houghton, Mich.

**Dyestuff Tables.** By G. SCHULTZ. 5th Ed. Lex. 8vo. 452 pp. Price, \$10.00. Weidmann, Berlin. (German.)

**Fuel, Solid, Liquid and Gaseous.** By J. S. S. BRAME. 8vo. 388 pp. Price, \$3.25. Edward Arnold, London.

**Glycerin, Manufacture of.** By FELD AND VORSTMANN. 2nd Ed. 12mo. Price, \$1.00. H. Desforges, Paris. (French.)

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**Metals, Precious, Progress in Leaching during the last Decades.** By ROSE BORCHERS. 8vo. 400 pp. Price, \$2.00. Wilhelm Knapp, Halle. (German.)

**New Journal: Internationale Zeitschrift fuer physikalisch-chemische Biologie.** By J. TRAUBE. J. Wilhelm Engelmann, Leipzig.

**Photomicrography, Handbook of.** By H. LLOYD HIND AND W. BROUGH RANDLES. 8vo. 292 pp. Price, \$2.00. Geo. Rutledge & Sons, London.

**Rubber: Its Sources, Cultivation and Preparation.** By HAROLD BROWN. 8vo. Price, \$1.50. John Murray, London.

**Silicates in Chemistry and Commerce.** By W. ASCH AND D. ASCH. 8vo. 476 pp. Price, \$6.00. D. Van Nostrand Co., New York. (Translation in English.)

**Soaps, Medicinal.** By WALTER SCHRAUTH. 8vo. 170 pp. Price, \$1.75. Julius Springer, Berlin. (German.)

**Steels, Steel-Making Alloys and Graphite, Rapid Methods for the Chemical Analysis of Special.** By CHARLES MORRIS JOHNSON. 3rd Ed. 8vo. 438 pp. Price, \$3.00. John Wiley & Sons, New York.

**Sugar Industry, Chemistry of the.** By OSKAR VOHNYZEK. 8vo. 676 pp. Price, \$5.00. Julius Springer, Berlin. (German.)

**Tanning Chemists and Leather Manufacturers, Pocketbook for.** By H. R. PROCTOR, EDMUND STIASNY AND HAROLD BRUMWELL. 8vo. 250 pp. Price, \$1.25. Th. Steinkopff, Dresden. (German.)

**Textile: Waterproofing of Fabrics.** By S. MIRZINSKI. 2nd Ed. Cr. 8vo. 132 pp. Price, \$1.25. Scott, Greenwood & Co., London.

**Triphenylmethyl.** By JULIUS SCHMIDLIN. Lex. 8vo. Price, \$2.20. Ferdinand Enke, Stuttgart. (German.)

**Water, Microscopy of Drinking.** By GEORGE C. WHIPPLE. 3rd Ed. 8vo. 409 pp. Price, \$4.00. John Wiley & Sons, New York.

### RECENT JOURNAL ARTICLES

**Acetyl-cellulose: Production, Characteristics and Utilization.** By WALTER VIEWEG. *Kunststoffe*, Vol. 4, 1914, No. 8, pp. 148-152.

**Acetyl-nitrocellulose and its Use for Celluloid.** By H. WISHIDA. *Kunststoffe*, Vol. 4, 1914, No. 8, pp. 141-142.

**Ammonia from Gas, Recovery of, by the Direct and Semi-Direct Sulfate Processes.** By M. DESMARETS. *Revue générale de chimie pure et appliquée*, Vol. 17, 1914, No. 7, pp. 115-122.

**Analysis, Micro-Elementary, of Organic Substances by Fritz Pregl's Method.** By J. V. DUBSKY. *Chemiker Zeitsung*, Vol. 38, 1914, Nos. 47 and 48, pp. 505-506, and 510-511.

**Iron, Electrolytic Reduction of, for Permanganate Titration.** By H. C. ALLEN. *Journal of the American Chemical Society*, Vol. 36, 1914, No. 5, pp. 937-949.

**Arsenic and Antimony, Organic Derivatives of.** By GILBERT T.

- MORGAN. *Pharmaceutical Journal*, Vol. 92, 1914, No. 2635, pp. 537-540.
- Arsenic, Quantitative Separation of, from Metals by Use of Hypophosphoric Acid.** By L. BRANDT. *Chemiker Zeitung*, Vol. 38, 1914, Nos. 43 and 44, pp. 461-463 and 474.
- Bronzes, Copper-Tin, Electrolytic Deposition of.** By R. KREMAN, C. TH. SUCHT, J. LORBER and R. MAAS. *Monatshcft fuer Chemie*, Vol. 35, 1914, No. 3, pp. 219-288.
- Coal, and the Chemistry of Its Carbonization.** By JOHN HARGER. *Journal of the Society of Chemical Industry*, Vol. 33, 1914, No. 8, pp. 389-392.
- Colloids.** By WOLFGANG OSTWALD. *Chemical Engineer*, Vol. 19, 1914, No. 4, pp. 133-137.
- Colloids in Effluents, Simple Method for the Determination of.** By R. MARC and K. SACK. *Kolloidchemische Beihefte*, Vol. 5, 1914, No. 8-10, pp. 375-410.
- Colorimeters, Two New.** By PAUL VERBEEK. *Zeitschrift fuer angewandte Chemie*, Vol. 27/I, 1914, No. 28, pp. 203-208.
- Concentration by Refrigeration of Liquid Vegetable Extracts.** By H. PARENTY. *Comptes rendus*, Vol. 158, 1914, No. 13, pp. 921.
- Drying Bagasse, Marcs, Sawdust, Peat, Etc.** By A. HUIILLARD. *Louisiana Planter*, Vol. 52, 1914, No. 16, pp. 251-252.
- Explosives: Blasting Gelatin, Some Notes and Theories.** By W. A. HARGREAVES. *Journal of the Society of Chemical Industry*, Vol. 33, 1914, No. 7, pp. 337-340.
- Fats, Unsaponifiable Constituents of Natural and Hardened.** By J. MARCUSON and G. MEYERHEIM. *Zeitschrift fuer angewandte Chemie*, Vol. 27/I, 1914, No. 28, pp. 201-203.
- Flame Reactions.** By W. D. BANCROFT and H. B. WEISER. *Journal of Physical Chemistry*, Vol. 18, 1914, No. 4, pp. 281-336.
- Gas, Coke-Oven and Blast-Furnace, Notes on the Utilization of, for Power Purposes.** By HEINRICH J. FREY. *Bulletin of the American Institute of Mining Engineers*, 1914, No. 88, pp. 665-694.
- Hydrogen-Peroxid, Synthesis of 100 Per Cent, by Silent Electric Discharges.** By PAUL MAX WOLF. *Zeitschrift fuer Elektrochemie*, Vol. 20, 1914, No. 7, pp. 204-219.
- Hydrogen, the Commercial Uses of.** By A. CROSSLEY. *Chemical Trade Journal*, Vol. 54, 1914, No. 1406, p. 497.
- Iron Corrosion by Dissolved Oxygen.** By J. W. COEB and G. DOUGILL. *Journal of the Society of Chemical Industry*, Vol. 33, 1914, No. 8, pp. 403-407.
- Iron and Steel, Influence of Copper on the Corrosion of.** By E. R. HAMILTON. *American Gas Light Journal*, Vol. 100, 1914, No. 16, pp. 246-247 and 250-252.
- Nickel, Electrodeposition of.** By C. W. BENNET, H. C. KENNEY and R. P. DUGLISS. *Journal of Physical Chemistry*, Vol. 18, 1914, No. 5, pp. 373-384.
- Nitro-bodies, Explosions of, and their Prevention.** By C. H. BORRMANN. *Chemiker Zeitung*, Vol. 38, 1914, No. 50, pp. 537-538.
- Paraffin, Liquid.** By J. WILCLIFFE PECK. *Pharmaceutical Journal*, Vol. 92, 1914, No. 2634, pp. 508-509.
- Patent Law, Plan of a.** By W. KARSTEN. *Zeitschrift fuer angewandte Chemie*, Vol. 27/I, 1914, No. 26, pp. 185-192.
- Peat, By-products from.** By F. M. PERKIN. *Chemical Trade Journal*, Vol. 54, 1914, No. 1403, p. 417.
- Petroleum and its Derivatives.** By DAVID T. DAY. *Oil, Paint and Drug Reporter*, Vol. 85, 1914, No. 17, pp. 18-19 and 33.
- Phosphorus, Red, Formation of, by the Oxidation of Phosphorus Vapor.** By KOHLSCHUETTER and FRUMKIN. *Berichte der deutschen chemischen Gesellschaft*, Vol. 47, 1914, No. 6, pp. 1088-1100.
- Picric Acid in Volumetric Analysis.** By A. SANDER. *Zeitschrift fuer angewandte Chemie*, Vol. 27/I, 1914, No. 26, pp. 192-194.
- Plating Baths, Use of Potassium Cyanid for.** By C. F. BURGESS and L. F. RICHARDSON. *Zeitschrift fuer angewandte Chemie*, Vol. 27/I, 1914, No. 30, pp. 211-212.
- Refuse Destructor, the Evolution of the.** By E. KOHLMANN. *Journal of the Society of Chemical Industry*, Vol. 33, 1914, No. 8, pp. 383-389.
- Shellac, Bleached: Its Production, Examination and Utilization.** By HANS WOLFF. *Kunststoffe*, Vol. 4, 1914, No. 8, pp. 143-145.
- Sodium from Caustic Soda by Electrolysis.** By BERNHARD NEUMANN. *Zeitschrift fuer angewandte Chemie*, Vol. 27/I, 1914, No. 26, pp. 195-200.
- Steel, Determination of Cobalt in.** By P. SLAWIK. *Chemiker Zeitung*, Vol. 38, 1914, No. 48, pp. 514-515.
- Steel, Manganese, Relation of Physical Properties to Microstructure and Critical Ranges, with Special Reference to.** By W. S. POTTER. *Bulletin of the American Institute of Mining Engineers*, 1914, No. 88, pp. 601-634.
- Tannin, Colloidalchemical Studies on.** By M. NAVASSART. *Kolloidchemische Beihefte*, Vol. 5, 1914, No. 8-10, pp. 299-374.
- Water Supply, The Croton: Its Quality and Purification.** By GEORGE W. FULLER. *Journal of the American Water Works Association*, Vol. 1, 1914, No. 1, pp. 135-187.
- Water Filtration Practice, Present Day.** By GEORGE A. JOHNSON. *Journal of the American Water Works Association*, Vol. 1, 1914, No. 1, pp. 31-80.
- Water-Sampling Bottle, Improved.** By RICHARD H. ENRICH. *Engineering Record*, Vol. 69, 1914, No. 19, pp. 543-544.
- Wood Pulp, Sulfite, Manufacture of.** By G. B. STEFFANSON. *Pulp and Paper Magazine of Canada*, Vol. 12, 1914, No. 9, pp. 259-264.
- Wood Pulp in Textil Manufacturing, The Utilization of.** By H. A. CARTER. *Canadian Textile Journal*, Vol. 31, 1914, No. 4, pp. 100-103.

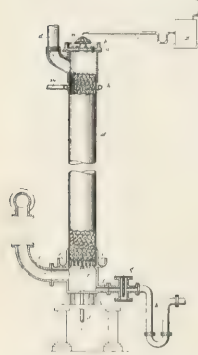
## RECENT INVENTIONS

By C. L. PARKER, Solicitor of Chemical Patents, McGill Building, Washington, D. C.

### Manufacture of Fuming Sulfuric Acid, or Oleum. Briggs and

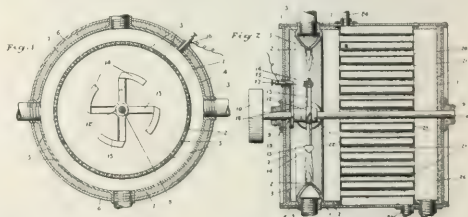
Merriman, Dec. 23, 1913. U. S. Pat. 1,082,301. In the use of this apparatus sulfuric acid having a strength of from 98 to 99.5 per cent flows from tank B over distributor n and through small openings c from which it falls in fine streamlets upon the packing of quartz in the tower A.

Air containing from 4 to 8 per cent of sulfuric anhydride enters the tower through pipe e and passes upward in contact with the thin films of sulfuric acid and is absorbed thereby, the resulting fuming sulfuric acid passing out of the tower through pipe f. The temperature in the tower is maintained at a desired point by spraying the outside of the tower with water from the ring nozzle k.



**Oxids of Nitrogen.** J. S. Island, Dec. 30, 1913. U. S. Pat. 1,082,529. In this apparatus the tubular ring 1 forms the positive electrode and the rotor 11 the negative electrode of means to produce an electric arc flame. Compressed air is

supplied to the tubular ring 1 and is forced at high velocity through minute openings 5 into the inner zone of the electric flame. The resulting gases are driven laterally by the angularly arranged blades 15 into contact with the surfaces of the cooling

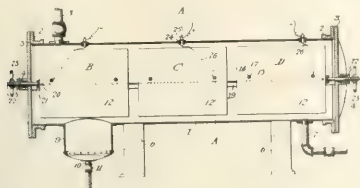


chamber 20 so that such gases are withdrawn from the middle and outer zones of the electric flame and cooled before there is any material dissociation of the nitric oxides formed in the inner zone.

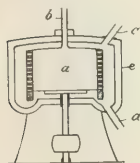
**Electrolytic Apparatus for the Clarification of Sugar Solutions.** H. McCubbin, Jan. 13, 1914. U. S. Pat. 1,084,556. The apparatus embodies means for treating sugar solutions electrically while they are passed through a container within which are electrodes exposing large surfaces for contact with the solutions during their passage through the container. Means are pro-



vided for adjusting the relative positions of the electrodes with respect to each other and the ends of the container are made

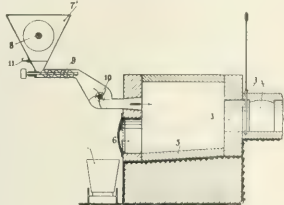


removable to permit the withdrawal of the electrodes for cleaning.

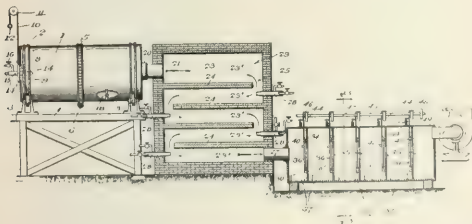


**Solid Fatty Substances from Oil.** J. Schlinck, Dec. 30, 1913. U. S. Pat. 1,082,707. Oils are hydrogenated by passing them over a catalyst secured within openings in the wall of the centrifugal drum *a*, in an atmosphere of hydrogen.

**Making Charcoal.** L. Félizat, Feb. 17, 1914. U. S. Pat. 1,087,486. Charcoal is produced from ground ligneous material, such as almond shells, peach or apricot kernels, olive husks, sawdust and the like by showering the waste material into a furnace heated to redness while at the same time introducing air to effect the complete combustion of the volatile products which are dissociated from the waste and which ignite on coming in contact with the red hot walls of the chamber. The residue remains on the bottom of the chamber in the form of incandescent charcoal. The hot gases are conducted under boilers to utilize the calorific power of the volatile products.



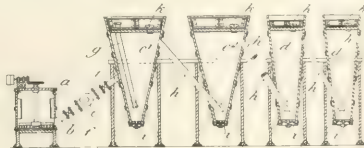
**Apparatus for Making White Lead.** R. A. Stewart, Feb. 24, 1914. U. S. Pat. 1,088,041. This apparatus is designed to produce a white commercial pigment from lead ores in one operation. The lead ore, such for example as sulfid ore, is first heated in the rotary drum 1. The products escaping into the supplementary roasting chamber 23 are gray or bluish by reason of



the presence of unoxidized lead particles, but in passing through chamber 23, which is heated by burners 28, it is converted into white lead so that the product passing out of the chamber 23 is a white commercial pigment which is recovered in the filter chamber 30. The products from the rotary drum 1 are drawn through the supplementary heating chamber and the filter chamber by means of a suction fan, 33.

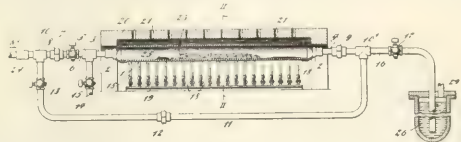
**Manufacture of White Lead.** F. R. Sharpe, Feb. 24, 1914. U. S. Pat. 1,088,460. The process consists in simultaneously

and continuously carbonating lead oxid, and separating with the aid of the carbonating agent the basic carbonate produced by a process resembling elutriation, i. e., the particles to be separated from heavier or less bulky particles are carried to the surface of a liquid in which the particles are suspended and are removed by the overflow of the liquid. This is done by using a series of



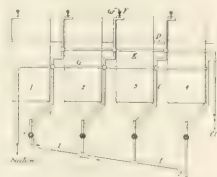
closed vessels communicating with each other in such a manner that the carbonating gas or gases pass through the liquid in each vessel, and at the same time the basic lead carbonate and the lead oxid undergoing carbonation are carried to the surface of the liquid in each vessel by the gas or gases passing through the liquid, and are carried forward from vessel to vessel as fresh liquid is admitted into the first of the series. In this manner the higher oxides of lead and the metallic lead are gradually separated.

**Economic Metallurgical and Chemical Process.** J. E. Bucher, Feb. 3, 1914. U. S. Pat. 1,086,019. Iron is heated with nitrogen and one or more powerful reducing elements such as sodium or potassium. A portion of the carbon in the iron combines with the purifying reagents to form a cyanogen compound



which is separated from the iron. In using the apparatus illustrated in practicing the process nitrogen is introduced into the retort through the pipe 24, the iron and reducing metal being previously heated to the boiling point of sodium or whatever reducing metal is employed.

**Asphalt from Crude Mineral Oil or Residum Thereof.** C. B. Forward, March 3, 1914. U. S. Pat. 1,088,692. Crude oil is subjected to a high temperature in a retort until all the volatile parts are separated from the asphalt base. The heavier portions of the volatile parts are condensed and mixed with the asphalt base, the mixture being heated in an open vessel until a desired adhesive condition is produced.



**Detinning.** F. von Kugelgen and G. O. Seward, Feb. 10, 1914. U. S. Pat. 1,086,921. Dry chlorin gas is circulated through tanks 1, 2, 3 and 4 containing tin scrap in various stages of detinning, the temperature being controlled to keep it below that at which the iron is attacked.

**Refractory Brick.** H. Wessling, March 3, 1914. U. S. Pats. 1,088,755 and 1,088,756. The brick is formed of fine particles of silica bounded together by a finely pulverized soapstone.

**Hydrometallurgy of Copper.** E. R. Weidlein, March 3, 1914. U. S. Pat. 1,089,096. Copper-bearing material is leached to obtain a copper solution containing not more than 3 per cent copper. The free sulfuric acid in the solution is neutralized and the copper precipitated substantially quantitatively by means of sulfur dioxide.

# MARKET REPORT

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR THE MONTH OF MAY, 1914

## ORGANIC CHEMICALS

Acetanilid.....	Lb.	21 1/2	@	22
Acetic Acid (28 per cent).....	C.	1.50	@	1.65
Acetone (drums).....	Lb.	10 1/2	@	11
Alcohol, denatured (180 proof).....	Gal.	35	@	37
Alcohol, grain (188 proof).....	Gal.	2.52	@	2.54
Alcohol, wood (95 per cent).....	Gal.	45	@	47
Amyl Acetate.....	Gal.	1.88	@	1.90
Aniline Oil.....	Lb.	10	@	10 1/2
Benzoic Acid.....	Lb.	23	@	25
Benzol (90 per cent).....	Gal.	23	to	25
Camphor (refined in bulk).....	Lb.	—	@	42 1/2
Carbolic Acid (drums).....	Lb.	7 1/2	@	9
Carbon Bisulfide.....	Lb.	6 1/2	@	7 1/2
Carbon Tetrachloride (drums).....	Lb.	30	@	31 1/2
Chloroform.....	Lb.	51	@	51 1/2
Citric Acid (domestic), crystals.....	Lb.	2.77	@	2.97
Dextrose (corn).....	C.	31	@	32
Dextrose (imported potato).....	Lb.	18	@	24
Ether (U. S. P., 1900).....	Lb.	8 1/2	@	9 1/2
Formaldehyde.....	Lb.	19	@	19 1/2
Glycerine (dynamite).....	Lb.	7 1/2	@	7 3/4
Oxalic Acid.....	Lb.	1.20	@	1.40
Pyrogallic Acid (bulk).....	Lb.	25	@	27
Salicylic Acid.....	Lb.	3 1/4	@	4
Starch (cassava).....	Lb.	1.99	@	2.10
Starch (corn).....	Lb.	4 1/2	@	4 3/4
Starch (potato).....	Lb.	7	@	8
Starch (rice).....	Lb.	21 1/2	@	22 1/2
Starch (sago).....	Lb.	49 1/2	@	51 1/2
Starch (wheat).....	Lb.	35	@	36
Tannic Acid (commercial).....	Lb.	—	@	30 1/2
Tartaric Acid, crystals.....	Lb.	—	@	30 1/2

## INORGANIC CHEMICALS

Acetate of Lead (brown, broken).....	Lb.	7 1/4	@	7 1/2
Acetate of Lime (gray).....	C.	1.50	@	1.55
Alum (lump).....	C.	1.75	@	2.00
Aluminum Sulfate (high-grade).....	C.	1.25	@	1.75
Ammonium Carbonate, domestic.....	Lb.	8	@	8 1/2
Ammonium Chloride, gray.....	Lb.	5 7/8	@	6 1/8
Aqua Ammonia (drums) 16°.....	Lb.	2 1/4	@	2 1/2
Arsenic, white.....	Lb.	3	@	3 1/8
Barium Chloride.....	Lb.	18 1/8	@	13 1/4
Barium Nitrate.....	Lb.	5	to	5 1/4
Barytes (prime white, foreign).....	Ton	19.00	@	23.50
Bleaching Powder (35 per cent).....	C.	1.2 1/2	@	1.25
Blue Vitriol.....	C.	4.80	@	5.00
Borax, crystals (bags).....	Lb.	3 3/4	@	4 1/2
Boric Acid, crystals (powd.).....	Lb.	7	@	8
Brimstone (crude, domestic).....	Ton	22.00	@	22.50
Bromine, bulk.....	Lb.	30	@	35
Calcium Chloride, fused.....	C.	60	@	65
Chalk (light precipitated).....	Lb.	4	@	4 1/2
China Clay (imported).....	Ton	14.00	@	16.00
Feldspar.....	Ton	8.00	@	12.00
Fuller's Earth, powdered, Foreign.....	Ton	16.00	@	17.00
Green Vitriol (bulk).....	C.	55	@	60
Hydrochloric Acid (18°).....	C.	1.15	@	1.65
Iodine (resublimed).....	Lb.	3.55	@	3.60
Lead Nitrate.....	Lb.	8	@	8 1/8
Litharge (American).....	Lb.	5 1/2	@	5 1/4
Lithium Carbonate.....	Lb.	65	@	70
Magnesium Carbonate.....	Lb.	21	@	35
Magnesite "Calcined".....	Ton	28.50	@	29.50
Nitric Acid, 36°.....	Lb.	37	@	41 1/2
Phosphoric Acid (sp. gr. 1.75).....	Lb.	20	@	24
Phosphorus.....	Lb.	45	@	1.00
Plaster of Paris.....	Bbl.	1.50	@	1.70
Potassium Bichromate, 50°.....	Lb.	6 1/2	@	7
Potassium Bromide.....	Lb.	39	@	40
Potassium Carbonate (calcined), 80 @ 85%.....	C.	3	@	3 1/4
Potassium Chlorate, crystals.....	Lb.	7 1/4	@	7 1/2
Potassium Cyanide (bulk), 98-99%.....	Lb.	19	@	22
Potassium Hydroxide.....	Lb.	4	@	4 1/8
Potassium Iodide (bulk).....	Lb.	2.95	@	3.00
Potassium Nitrate (crude).....	Lb.	4	@	5 1/4
Potassium Permanganate (bulk).....	Lb.	37.50	@	10
Quicksilver, Flask (75 lbs.).....	Lb.	6	@	6 1/4
Red Lead (American).....	Lb.	55	@	65
Salt Cake (glass makers').....	C.	55	@	65

Silver Nitrate.....	Oz.	37	@	40
Soapstone in bags.....	Ton	10.00	@	12.00
Soda Ash (48 per cent).....	Lb.	67 1/2	@	72 1/2
Sodium Acetate.....	Lb.	34	@	41 1/8
Sodium Bicarbonate (domestic).....	C.	1.00	@	1.10
Sodium Bicarbonate (English).....	Lb.	24	@	3
Sodium Bichromate.....	Lb.	41	@	5
Sodium Carbonate (dry).....	C.	60	@	80
Sodium Chlorate.....	Lb.	7 1/4	@	7 1/2
Sodium Hydroxide, 60 per cent.....	C.	1.55	@	1.57 1/2
Sodium Hyposulfite.....	C.	1.30	@	1.60
Sodium Nitrate, 95 per cent, spot.....	C.	—	@	2.20
Sodium Silicate (liquid).....	C.	65	@	1.50
Strontium Nitrate.....	Lb.	6 1/4	@	7
Sulfur, Flowers (sublimed).....	C.	2.20	@	2.60
Sulfur, Roll.....	C.	1.85	@	2.15
Sulfuric Acid, 60° B.....	C.	85	@	1.00
Talc (American).....	Ton	15.00	@	20.00
Terra Alba (American), No. 1.....	C.	75	@	80
Tin Bichloride (50°).....	Lb.	11 1/2	@	12 1/2
Tin Oxide.....	Lb.	38	@	49
White Lead (American, dry).....	Lb.	54 1/2	@	55 1/2
Zinc Carbonate.....	Lb.	8 1/2	@	9
Zinc Chloride (granulated).....	Lb.	4 1/2	@	5
Zinc Oxide (American process).....	Lb.	5 1/2	@	6 1/2
Zinc Sulfate.....	C.	2.35	@	2.70

## OILS, WAXES, ETC.

Beeswax (pure white).....	Lb.	45	@	47
Black Mineral Oil, 29 gravity.....	Gal.	13 1/2	@	14
Castor Oil (No. 3).....	Lb.	8	@	8 1/2
Ceresin (yellow).....	Lb.	12	@	22
Corn Oil.....	C.	6.55	@	6.60
Cottonseed Oil (crude), f. o. b. mill.....	Gal.	45	@	46
Cottonseed Oil (p. s. y.).....	Lb.	7	@	7 1/2
Cylinder Oil (light, filtered).....	Gal.	21 1/2	@	32
Japan Wax.....	Lb.	12	@	13
Lard Oil (prime winter).....	Gal.	92	@	95
Linseed Oil (raw).....	Gal.	49 1/2	@	52
Menhaden Oil (crude).....	Gal.	nominal		
Neatsfoot Oil (20°).....	Gal.	96	@	98
Paraffine (crude, 120 & 122 m. p.).....	Lb.	3 1/4	@	3 1/2
Paraffine Oil (high viscosity).....	Gal.	27	@	28
Rosin ("F" grade) (280 lbs.).....	Bbl.	4	@	50
Rosin Oil (first run).....	Gal.	—	@	27
Shellac, T. N.....	Lb.	15	@	16
Spermaceti (cake).....	Lb.	30	@	31
Sperm Oil (bleached winter), 38°.....	Gal.	70	@	71
Spindle Oil (No. 200).....	Gal.	18	@	19
Stearic Acid (double-pressed).....	Lb.	9	@	12
Tallow (acidless).....	Gal.	65	@	66
Tar Oil (distilled).....	Gal.	30	@	31
Turpentine (spirits of).....	Gal.	47	@	47 1/2

## METALS

Aluminum (No. 1 ingots).....	Lb.	17 1/2	@	18
Antimony (Hallet's).....	Lb.	64 1/2	@	74 1/2
Bismuth (New York).....	Lb.	2.05	@	2.10
Bronze powder.....	Lb.	50	@	3.00
Copper (electrolytic).....	C.	14.10	@	14.20
Copper (lake).....	C.	14.25	@	14.35
Lead, N. Y.....	C.	3.90	@	—
Nickel.....	Lb.	50	@	55
Platinum (refined).....	Oz.	43.50	@	44.50
Silver.....	Oz.	58	@	58 1/4
Tin.....	C.	32.95	@	37.00
Zinc.....	C.	5.15	@	5.20

## FERTILIZER MATERIALS

Ammonium Sulfate.....	C.	2.80	@	2.85
Blood, dried.....	Unit	3.35	@	—
Bone, 4 1/4 and 50, ground, raw.....	Ton	30.00	@	—
Calcium Nitrate (Norwegian).....	C.	2.05	@	2.15
Castor meal.....	C.	3.35	@	—
Fish Scrap, domestic, dried.....	Unit	nominal		
Phosphate, acid, 16 per cent bulk.....	Ton	7.00	@	—
Phosphate rock; f. o. b. mine.....	Ton	2.25	@	2.50
Florida land pebble, 68 per cent.....	Ton	5.00	@	5.50
Tennessee, 70-80 per cent.....	Ton	39.07	@	—
Potassium, "muriate," basis 80 per cent.....	Unit	0	@	13 1/4
Pyrites, furnace size, imported.....	Unit	3.35	@	10
Tankage, high-grade.....	Unit	3.35	@	10

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## TABLE OF CONTENTS

EDITORIALS:		A Manostat for Use in Gas Analysis. By Harvey N. Gilbert.....	585
Nitrates in Colorado Soils.....	532		
ORIGINAL PAPERS:		ADDRESSES:	
Electric Furnaces for Heating Steel. By Alcan Hirsch. Study of Authentic Samples of Gum Turpentine. By A. W. Schorger.....	533	The Excessive Quantities of Nitrates in Certain Colorado Soils. By Wm. P. Headden.....	586
The Hypochlorite of Lime Treatment of a Municipal Water Supply and a Study of Certain Resistant Bacteria. By Stanley Judson Thomas.....	541	The Workings of the California Insecticide Law. By Geo. P. Gray.....	590
The Radioactivity of the Waters of Saratoga Springs, New York. By Richard B. Moore and C. F. Whittemore.....	548	CURRENT INDUSTRIAL NEWS: Correction; Measuring Rapidly Changing Temperatures; The Australian Coal Trade; A New Recording Device; The Kongsberg Silver Works, Norway; Production of Zinc in Europe, 1913; Mining in China; The Oil Resources of the British Empire; Coal Storage and Gas Manufacture; The Corrosion of Iron by Dissolved Oxygen; The Lighting of Rio de Janeiro; The Utilization of Sulfite-Cellulose Waste; Canadian Coke Ovens; German and English Exports of Ammonium Sulfate in 1912 and 1913; Destruction of an Artificial Leather Factory.....	594
A New Method for the Determination of Hydrocyanic Acid and the Alkali Cyanides. By G. E. F. Lundell and J. A. Bridgman.....	552	AMERICAN INSTITUTE OF CHEMICAL ENGINEERS: Account of Meeting; Papers; Excursions.....	598
A Method for the Rapid Quantitative Analysis of Bronze and Brass. (Pb, Cu, Sn, Sb, Fe and Zn.) By Richard Edwin Lee, John P. Trickey and Walter H. Fegeley.....	553	Some Professional Obligations. By M. C. Whitaker.....	599
The Chemical Evaluation of Wood for Pulp. By M. L. Griffin.....	554	NOTES AND CORRESPONDENCE: The Invention of Celluloid; Symposium on the Recovery of Wool Grease; Guaranteed Chemicals; Toxicity of Various Wood Preservatives—A Note; Note on Meaning of "Impurities" and How They Should be Determined in Grease, Tallow, Etc.; Test of Gila River Natural Aluminum Sulfate in Water Purification; The Effects of the Ensilage Process on the Solubility and Metabolism of Floats; Mine Inspectors Institute of the U. S.; Ninth International Congress of Applied Chemistry; Van't Hoff Fund for the Endowment of Research in Pure and Applied Chemistry; American Chemical Society—Annual Meeting; A. C. S. Directory, 1914; Industrial Chemists and Chemical Engineers—A. C. S.—Committee on Alum Specifications—Correction and Notice; The Differentiation of Natural and Oil Asphalts—Correction.....	601
Determination of Carbon in Soils and Soil Extracts. By J. W. Ames and E. W. Gaither.....	556	PERSONAL NOTES.....	607
The Melting and Solidifying Points of Mixtures of Fatty Acids and the Use of These Points to Determine the Composition of Such Mixtures. By E. Twitchell.....	560	GOVERNMENT PUBLICATIONS.....	608
The Specific Heat of Milk and Milk Derivatives. By Arden R. Johnson and B. W. Hammer.....	561	BOOK REVIEWS: Engineering Thermodynamics; Das Lebensmittelgewerbe; Exercises in Gas Analysis; Treatise on the Ceramic Industries; Untersuchung der Kohlenwasserstoffole und Fette; Coal Tar Distillation; Taschenbuch für die anorganischchemische Grossindustrie; Details of Cyanide Practice; Taschenbuch für Gerberlei-Chemiker.....	611
Note on the Precipitation of Lactalbumin in Cows' Milk. By W. O. Walker and A. F. Grant Cadenhead.....	564	NEW PUBLICATIONS.....	614
The Absorption of Certain Radicals by Leaves in Varying Stages of Decay, and the Effect of Leaves on the Absorption of These Radicals by a Soil. By H. A. Noyes.....	569	RECENT INVENTIONS.....	615
Distribution of Certain Constituents in the Separates of Loam Soils. By L. A. Steinkoenig.....	573	MARKET REPORT.....	616
The Preparation of "Neutral" Ammonium Citrate. By Ermon D. Eastman and Joel H. Hildebrand.....	574		
A Procedure for Separating Organic Ammoniates from the Mineral Portion of Commercial Fertilizers. By C. H. Jones and G. F. Anderson.....	576		
The Availability of Nitrogen in Kelp. By John A. Cullen.....	577		
LABORATORY AND PLANT:			
Pitot Tubes for the Measurement of Gas Velocities. By Andrew M. Fairlie.....	580		
The Non-Uniformity of Drying Oven Temperatures. By Lorin H. Bailey.....	581		



## EDITORIALS

### NITRATES IN COLORADO SOILS

In a number of publications, Headden, of the Colorado Experiment Station, has shown that the soils of Colorado contain in various places excessive quantities of nitrates. Ordinarily good, cultivated soil he found to contain from 5 to 8 parts of nitrates per million of the dry soil. In the nitrate areas, however, many thousand parts per million of nitrate nitrogen were found. In one sample of surface soil there were found 6.54 per cent of sodium nitrate or nearly 11 tons in an acre of ground taken to the depth of 1 inch. The high nitrate content is generally found in spots but these spots often grow to cover large areas. Thus what was five or six years ago a spot has grown to involve as much as six, eight, and more acres. The nitrates are present in large quantities in numerous areas scattered over 300 to 400 square miles. The orchards in a single district including 50 square miles have been practically ruined.

These observations and studies are of so great interest and importance to agricultural investigators that it is a matter for congratulation that Professor Headden has been prevailed upon to furnish his own statement of his work in other columns of *THIS JOURNAL*.

A brief repetition of the principal results, however, can be given here.

As a result of the nitrate accumulation, in a number of places large areas have been made sterile. Whether large or small the affected areas are characterized by a brown coloration, mealiness of the soil, a high nitrate content, and, unless the nitrate content is excessively high, by the presence of nitrogen-fixing organisms such as azotobacter. With the increase in the colored patches and the amount of nitrate, the crops covering the involved areas rapidly deteriorate and even die out. The greatest injury has been to the apple orchards though other crops such as alfalfa, sugar beets, etc., have been seriously injured. The trouble is common to several sections of the State. Sometimes it has occurred in light sandy loams, sometimes in clay soil, sometimes in comparatively low-lying lands, again on hillsides.

Sodium chloride is also present in large amounts in the Colorado soils. According to Headden, however, this salt though injurious in large amounts does not produce any of the characteristic phenomena observed in the dying orchards, while application of large quantities (5 pounds to a four-year-old tree) of sodium nitrate to an experimental orchard and irrigating to bring the nitrate in contact with the feeding roots reproduced the identical phenomena noticed in the other orchards where the trees had died. It would seem then that whatever contributing cause there may be, the sodium nitrate present in the soil is sufficient to bring about the deterioration and death of trees and crops in the affected areas.

Though the presence of the highly excessive quantities of nitrate which bring about loss of general productiveness involves only a small percentage of the arable Colorado soil, the formation of these high nitrate areas

in the various sections of the State is a problem of great importance and concern to agriculturalists of Colorado and a phenomenon of the greatest interest to chemists and bacteriologists.

In soils in general the formation of nitrates is brought about by several soil microorganisms which fix nitrogen from the air, form ammonia from more complex nitrogenous compounds, and form nitrites and nitrates from ammonium compounds. As a rule the nitrates in soil are small in amount. Accordingly, the Colorado situation is exceedingly remarkable.

As to the origin of the nitrates there is some dispute. Headden holds that the abnormal accumulation of nitrates cannot be due to evaporation of surface waters containing nitrates coming from a distance from soil or shale since: (1) neither soil nor shale contain a supply of nitrogen adequate to account for the formation of nitrates found; (2) the natural water and the irrigation water contain only small quantities of nitrates; (3) the brown nitrate-containing areas often occur at a high elevation. In addition the accumulation of nitrates may occur on well drained lands, where the water level is some distance from the surface. Headden's positive conclusion is that the source of the nitrates is the atmosphere, the nitrogen of which is fixed by azotobacter. In support of Headden's conclusions, Sackett found that the Colorado soils were rich in azotobacter which had the power to fix nitrogen in solution and in soil and fixed it at a rate sufficient to account for the nitrates found in the soil, provided the nitrogen is nitrified by other organisms.

Sackett likewise found that the Colorado soils have a higher ammonifying power than have ordinary soils and a higher nitrifying power and comes to the conclusion that the excessive nitrate present in certain Colorado soils has resulted from the combined action of nitrogen-fixing, ammonifying, and nitrifying organisms. Since the Colorado soils are poor in organic matter and azotobacter requires a supply of carbohydrate for its development and the fixation of nitrogen, it seemed difficult to account for the source of energy necessary to support such a rich nitrogen-fixing flora as possessed by the soils in question. Robbins, however, found the algae flora especially the blue-green algae (*Cyanophyceae*) to be very abundant. It is well known that certain bacteria and algae enter into symbiotic relationship in which the algae furnish the bacteria with a suitable form of carbohydrates. The algae in the Colorado soil may furnish the necessary food material for azotobacter.

An opposing view is that of Stewart and Greaves (Agric. Expt. Sta., Utah, *Bull.* 114) that the nitrates of the Colorado soil have their origin in the country rocks. The fact that in widely distributed areas in the arid west deposits of nitrates are found which do owe their origin to leaching from the country rock, supports, in their opinion, the theory that the excessive quantities of nitrates found in the soil of Colorado owe their origin

to the same source as do the other water-soluble salts. Further, Stewart and Greaves claim that in Headden's work wherever there was a variation in nitric nitrogen there was a variation in chlorine in the same direction which would seem to indicate a common origin of the nitrates and chlorides. To take a particular case, they point out that where there was an increase in the surface soil of 561 pounds of nitrates per acre two inches of soil during the years from 1909-1911 there was an increase of 10,430 pounds or over five tons of chlorine. In another case, referred to by Headden in Bulletin 155, the nitrate nitrogen increased from 1907 to 1911 from a trace to 621 pounds. In the same interval the chlorine content increased 236,883 pounds. They come to the inevitable conclusion that there must be an upward movement of the water-soluble salts, that the chlorides must come from the ground water. Accordingly, they ask the pertinent question, "Why may not the nitric nitrogen be accounted for in the same way?" Evaporation of the soil water would explain the deposit of nitrates since according to their calculations, assuming the optimum amount of water, 18 per cent, to be present, only one-half year of maximum evaporation would deposit the quantity of nitrogen actually deposited in two years. If the ground water contains only 74.48 parts per million of chlorine as computed by Headden, the evaporation would account for only 203 pounds of chlorine, whereas the actual amount found in the samples mentioned was

many times greater. So they conclude that the ground water has a greater concentration in chlorine and nitrogen than assumed and that both accumulate in the surface soil by evaporation of the water.

Stewart and Greaves do not deny that nitrogen fixation may take place to a certain extent in the Colorado soil and in some places to an appreciable degree, but do hold that whatever theory accounts for the accumulation of chlorides in the Colorado soils must account also for the greater portion of the nitrates present. To these arguments of Stewart and Greaves, Headden has opposed numerous objections which cannot be considered here. Suffice it to say, that while there can be no possible question of the occasional occurrence of abnormal quantities of nitrates in the "alkali" soils of Colorado, the origin of these excessive nitrate accumulations is not settled.

In their endeavor to explain the origin of the nitrate and to remedy the conditions as they arise, the various investigators should meet with general encouragement. It is greatly to be desired that the nitrate formation should be considered from all viewpoints to the end that accumulating data and suggestions may the more quickly develop an harmonious conclusion, to the advantage of practical agriculture and to the increase of the sum total of human knowledge.

BUREAU OF SOILS  
DEPARTMENT OF AGRICULTURE  
WASHINGTON

M. X. SULLIVAN

## ORIGINAL PAPERS

### ELECTRIC FURNACES FOR HEATING STEEL<sup>1</sup>

By ALCAN HIRSCH

Received May 25, 1914

The field of usefulness of the electric furnace for metallurgical purposes is so extensive that it is deemed advisable to limit the scope of this paper to a discussion of electric furnaces used for heating steel for the various kinds of heat treatment, forging and enameling. A broad view of the development of electric furnaces by the writer and his associates during the past year, together with details of design, construction and operation, as determined by them are presented herein. The essential data only are given as it is believed that extensive details are likely to lead to confusion. It is thought such a presentation of basic principles will make the paper of more value to users of electric furnaces than an extended report of all the data collected.

Prior to 1913 attempts were made to put forth furnaces for metallurgical purposes, but except for the very small furnaces, these cannot be considered as having had commercial success. The facts which form the basis of this paper occurred under the writer's observation and are practically exclusively gathered from his experience of the past year.

By reason of industrial practice and certain other

limitations, both fuel and electric furnaces can be divided into two classes:

I—Furnaces operating above 1800° F. Forge furnaces are the main and most important division of this class.

II—Furnaces operating below 1800° F. This class comprises furnaces for practically all heat treating as well as enameling. Although furnaces operating at the lower temperatures will be considered first it must be borne in mind that the greater part of the principle and theory underlying the construction and operation of moderate and low temperature furnaces also applies to the higher temperature furnaces.

#### TRANSFERENCE OF HEAT FROM HEATING MEDIUM TO METAL

The metal resting on the hearth of the furnace receives its heat in several different ways: (1) From the brickwork in the furnace in contact with the metal; (2) by conduction from the products of combustion; (3) by radiation from the hot walls, roof and incandescent particles in the burning gases. Generally speaking, in the fuel-fired furnaces, each of these paths delivers heat of the same order of magnitude, but usually the amount of heat passing by means of brick and metal in contact is less than that by any other path. If only a small portion of the heat passes into the metal by direct contact with the brick, the rate of heating in all except thin pieces is quite slow. More frequently than is generally supposed this path of heat trans-

<sup>1</sup> Author's abstract of report on research carried out under a Carnegie Fellowship granted by the Iron and Steel Institute of Great Britain. The complete report of this work was presented at the Annual Meeting of the Institute, May 7, 1914.

fer is the determining factor in the rate of heating. An excellent example of this kind was brought to the writer's attention where die blocks were being heated. In this instance the furnace was heated to a sufficiently high temperature so that the heat content of the brick work was sufficient to supply the necessary heat to raise the blocks to the desired temperature. Sometimes the fuel was allowed to run sparingly throughout the operation, while at other times it was shut off entirely after the block was placed in the furnace.

#### ATMOSPHERE IN FURNACES

The atmosphere of fuel-fired furnaces is exceedingly uncertain. Slight variations in conditions have been found to make marked variations in results, and as the atmosphere is capable of a great many variations, it is, therefore, quite difficult to maintain it at a definite composition. With oxidizing conditions the formation of scale occurs, while in a reducing atmosphere local carburization results from the sooty flames. In the production of high-grade steel the condition of hearth atmosphere is, of course, exceedingly important.

The electric furnace provides in many respects just what the fuel furnace lacks; *i. e.*, a means for the transference of heat in a very effective manner, and a furnace atmosphere which is not only of a very desirable composition, but which is absolutely dependable. This atmosphere is usually of a slightly reducing nature, caused by the presence of carbon monoxide, due to the combustion of the graphite or carbon resistor which liberates the electrical energy in the form of heat. In some furnaces having more than one door, or operated with doors open all the time, the atmosphere may be neutral. It is due to these neutral or reducing conditions that the formation of scale is greatly minimized. The writer has in mind an electric furnace which was operated with a loss of scale amounting to eighty or even ninety per cent less than was occasioned by the employment of an oil-fired furnace for the same work. For special work where an oxidizing atmosphere is required, as for instance in enameling, this is easily accomplished in the electric furnace by employing a muffle, the resistors being placed in any desired position on the outside of the muffle.

#### ELECTRIC FURNACES FOR TEMPERATURES BELOW 1800° F.

**FURNACES WITH METALLIC RESISTORS**—The industrial electric furnaces of this type which have obtained commercial success have employed a resistance wire or ribbon as the heating element. The limitations of these wire or ribbon-wound furnaces are quite marked, generally speaking, as regards both temperature and capacity. As will be shown subsequently, temperature and capacity of a furnace are closely interrelated. This interrelation of temperature and capacity, however, is not of so much consequence in the small furnaces where the combined wall and door losses are considerably in excess of the heat actually utilized in raising the metal to the desired temperature. The capacity of the metallic resistor furnace is at most but a very few kilowatts. Furnaces with a larger capacity would be quite out of the question because of the cost of the resistance element due to the large amount of

wire required and the expense of winding. The furnaces are, therefore, limited to productions of small size and also to rather moderate temperatures as danger of burning out due to overheating is quite imminent. For small furnaces, however, this type has proven quite satisfactory in a large quantity of work of an experimental nature.

**FURNACES EMPLOYING NON-METALLIC RESISTORS** comprise two types: (1) Those where the metal to be heated is in contact with the resistor; (2) those where the metal to be heated is out of contact with the resistor.

Furnaces of the first class have had but one commercial example, and that has had varying success. This is the bath furnace<sup>1</sup> which employs a conducting bath of salt, usually barium chloride and potassium chloride, which is fused by the passage of the current through it. The steel to be heated is immersed in this bath of fused salts. This type of furnace appears to the writer to be too limited for extensive industrial application, and, therefore, will be given only this brief mention.

Furnaces of the second class, those employing non-metallic resistors, where the metal is heated out of contact with the resistor, hold forth much promise for future development, in the opinion of the writer. Recent experience with their operation has demonstrated their suitability to many kinds of work. In general, furnaces of this class appear to the casual observer, very similar to the fuel-fired furnaces, save for the fact that instead of equipment for burning fuel, electrical equipment will be noted. The electric current is brought to the furnace by suitable cables which are connected to electrodes projecting from the furnace. These electrodes run through the furnace wall and carry the current to the resistor which liberates, in the form of heat, the electrical energy put into the furnace. The resistor is of a refractory conducting material, such as graphite, usually in granular form, and has a cross-section of 30 to 100 square inches according to the current desired. The resistors are usually placed beneath the hearth, the heat from them being communicated through the hearth to the metal.

For the design of a heat-treating furnace to operate at a hearth temperature of 1800° F., or less, the following data have been found necessary for the preliminary calculation of the major points of design:

- 1—The hearth dimensions.
- 2—The production of metal per unit of time.
- 3—The maximum amount of metal on the hearth at any time.
- 4—The desired temperature.
- 5—Time for charging and discharging.

**LOCATION OF RESISTOR**—The first step in the design is the approximation of the location of the resistor, but this depends somewhat on the physical characteristics of the material employed for the resistor. Resistors placed in the furnace in granular or similar form have been much more extensively employed in the larger furnace than any other kind. Rods of

<sup>1</sup> An article on this furnace by L. M. Cohn will be found in the *Electrotech. Zeit.*, Aug. 2, 1906.



graphite and also of other materials, metalloids as well as the characteristic non-metallic materials, have been tried for use as resistors. Although some of these will undoubtedly find commercial fields, as yet nothing has proven satisfactory in this direction. Attention, therefore, will be confined to granular or similar materials, of which granular graphite has served most satisfactorily.

For the usual type of electric furnace work of this class the location of the resistor is logically in the base of the hearth. For a small proportion of the furnaces, however, resistors can be placed elsewhere advisably. These positions are along the side of the hearth and possibly even along the top. Furnaces requiring resistors in these latter locations are those taking piles of sheet metal or pots of materials, and the like. However, with one layer of pieces, which rests directly on the hearth, the location of the resistor had best be exclusively in the base. The reasons for this are: (1) heat has a tendency to ascend rather than to descend; (2) contact between hot brick and the metal to be heated facilitates heating; (3) the design is facilitated as will be subsequently developed. When the resistors are placed in the base of the furnace they are put in troughs of suitable refractory material and usually, but not always, covered partly or completely with brick or tile, which forms the hearth.

**SHAPE OF RESISTORS**—The shape of the resistors can be exceedingly varied. They may be straight, U-, S-, T-, or Y-shaped. They may be electrically connected in series or parallel, or some in series and others in parallel. They may be permanently electrically connected, or they may be capable of various electrical arrangements by switching.

#### PERMANENTLY ELECTRICALLY CONNECTED RESISTORS

Furnaces with these resistors are constructed so that they must be operated in one manner, at all times from the point of view of electrical arrangement.

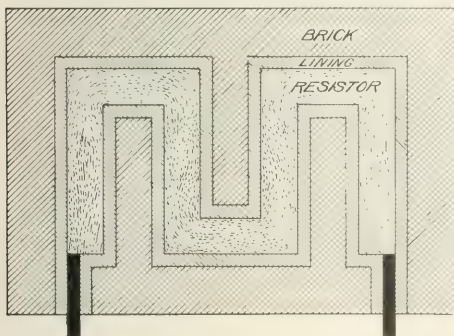


FIG. I.—SERPENTINE RESISTOR FOR MODERATELY LARGE FURNACES

In practically all furnaces of this class either a serpentine or U-shaped resistor may be employed, but two or more straight resistors connected either in series or in parallel may be used instead. Fig. I shows the serpentine resistor which has been employed in moderately large furnaces only, it being impossible to adapt this type to the smaller furnaces. The U-shaped

resistor shown in Fig. II has been employed in furnaces of any size but has some limitations which will be considered later.

**ELECTRICAL LOAD**—There are several ways to determine the electrical load for a given furnace, but they all resolve themselves into one method, which is the only one deemed sufficiently practical to be given consideration in this paper. Only furnaces of 200 kilowatts capacity or less will be considered and it may be said that furnaces for heat treating larger than this are exceedingly rare. The electrical load is the sum of three factors: (1) the electrical equivalent of the amount of heat necessary to raise the metal to the required temperature; (2) the electrical equivalent of the loss of heat through the walls; (3) the electrical equivalent of the loss of heat through the door, in consideration of the fact that this is alternately opened and closed. Since the power factors of furnaces of this size are from 97 to 99 per cent, they can be neg-

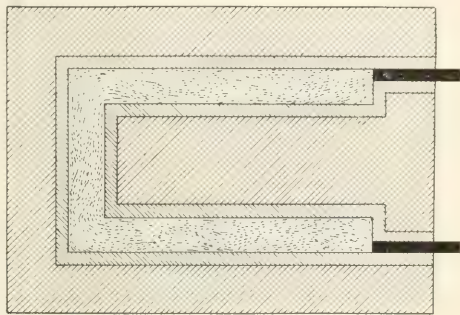


FIG. II.—U-SHAPED RESISTOR

lected in the calculation of the necessary wattage. From the data in Table I the watts necessary to operate any particular furnace may be approximated quite closely. The door loss shows the watts passing through the door opening if the door is open all the time. If the door is open only half the time, only half the amount given in the table should be taken, and so on in proportion. The wall upon which the wall loss figures are based is 12 inches thick, consisting of 9 inches of silica brick and 3 inches of kieselguhr. By actual practice this has been found to be a convenient standard. As an example of the method of calculation, the electrical load for a particular furnace will be determined. Assume the following data for this illustrative case:

- 1—Outside dimensions—4 ft.  $\times$  4 ft.  $\times$  6 ft. long.
- 2—Production—500 pounds of steel per hour.
- 3—Temperature—1700° F.
- 4—Door—2 sq. ft., open 40 per cent of the time.

This furnace had a total outside area of 128 sq. ft. The table shows a wall loss of 0.060 watt per sq. ft., making a total loss of 7.68 k.w. for the walls, top and base. The door loss would be 10.0 k. w. if the door were open all the time, but it being open but 40 per cent of the time, the loss is 4.0 k. w. As 0.0881 k. w. is required to raise 1 lb. of steel to 1700° F. from 60° F. in 1 hr., 500 lbs. per hr. would require 44.05 k. w.

TABLE I

Temperature of operation		Kilowatts to raise	Wall losses, in k. w.	Door loss(b)
° F.	° C.	1 lb. per hr. from 60° F.	per sq. ft. outside surface	in k. w. per sq. ft.
1000	538	0.0366	0.035	0.6
1100	594	0.0460	0.039	0.9
1200	649	0.0527	0.042	1.3
1300	704	0.0597	0.046	1.7
1400	760	0.0668	0.049	2.3
1500	815	0.0733	0.053	3.0
1550	843	0.0765	0.055	3.5
1600	870	0.0796	0.056	3.9
1650	898	0.0840	0.058	4.5
1700	926	0.0881	0.060	5.0
1750	954	0.0926	0.062	5.6
1800	982	0.0970	0.064	6.3
1850	1010	0.0994	0.065	7.1
2400	1316	0.122	0.083	20.0

(a) Based on wall 12 inches thick (9 inches of silica + 3 inches of kieselguhr).

(b) Door open all the time.

Thus it will be seen that this furnace will require 55.7 k. w. for operation. No factor of safety need be applied to this figure if the conditions selected are at the maximum. On the contrary, if these are normal operating conditions a factor of safety should be applied according to the possibilities of greater demands being made on the furnace.

After calculating the number of kilowatts necessary for operation, the length of the resistor is approximated in order to determine the voltage. With granular graphite<sup>1</sup> experience has shown that the most satisfactory voltage is equivalent to 1½ volts per inch length of the resistor. From this voltage and the wattage as computed above, the number of amperes may be easily determined.

**E. M. F. REQUIREMENTS**—The electrical resistance of a resistor in a furnace cannot be sufficiently closely predicted to warrant calculating the size of the resistor with a very great degree of certainty. Of necessity, therefore, the exact voltage which will be required for a furnace to take a certain number of kilowatts can be determined only approximately. A provision for obtaining various voltages is, therefore, necessary, and a transformer with several taps is ordinarily employed for this purpose. However, it is perfectly possible to provide a variable voltage generator for the same purpose. Since the precise production of steel for a given furnace cannot be very closely ascertained, and since, in most cases, different productions are desired at different times, it is absolutely necessary that provision be made for altering the kilowatt input at will of the operator.

The usual and satisfactory method of meeting these requirements appears to be the employment of a transformer with 10 to 15 taps. Usually 13 is a satisfactory number, having a range of voltages on the secondary from a minimum equivalent to one volt per inch length of the resistor to a maximum equivalent to two volts per inch length of the resistor. The various taps on the transformers used in most instances have given voltages which are in arithmetical progression, but it is the opinion of the writer that a progression of voltages in unequal steps is best suited for the work. For the purpose of making provision for the uncertainty of the resistance of the resistor, the voltages would logically be chosen in arithmetical progression. For purposes of regulation, however, since the kilowatt in-

put increases as the square of the voltage, it would appear, from this point of view, that the voltage steps should be graduated to best meet this condition. The two conditions must be met, and the most satisfactory arrangement is to make the steps in such progression that the difference of the kilowatt input on adjacent taps in the higher voltages will not be so very much larger than on the adjacent taps on the lower voltages. Accordingly, a satisfactory range of potentials on a transformer with 13 taps would have voltages equivalent to the following, per inch length of the resistor: 1.00, 1.10, 1.20, 1.29, 1.38, 1.47, 1.56, 1.64, 1.72, 1.80, 1.87, 1.94, 2.00.

#### ELECTRICAL REGULATION WITHOUT TRANSFORMER

A method<sup>1</sup> for obtaining this regulation and adjustment without the use of a transformer has been devised in the writer's laboratory very largely through the work of Mr. Richard S. Bicknell. In this type of furnace several resistors are employed, which are not permanently electrically connected, and which by means of suitable switches may be connected in various ways while the furnace is in operation. They may be arranged in series, in parallel or in any combinations necessary to effect the desired regulation. In other words, this is regulation by altering the resistance of the resistor as contrasted with the aforementioned method where regulation was effected by altering the voltage impressed upon the resistor. As will be shown subsequently this type of regulation is particularly adapted to furnaces having 10 sq. ft. of hearth area or over. An example of a furnace capable of such regulation is shown in Fig. III. With these four resistors in this particular furnace it is possible to obtain 110 inches in length of resistor, or equivalent of same, in the circuit at one time, and 220 inches in length of resistor at another. A large number of intermediate lengths of resistor between this maximum and minimum figure may also be placed in operation. This particular furnace is designed to operate on 220 volts and it will be readily seen that the maximum voltage obtainable per inch of resistor is two volts and the minimum is one volt. A quite surprisingly large number of intermediate lengths of resistor are obtained by employing the four T-shaped resistors, as shown. The length of the resistor is, of course, merely another way of stating the resistance of the furnace. These T-shaped resistors have each three unequal legs. Resistors *A* and *D* are similar and *B* and *C* are similar, but *A* and *B* have corresponding legs of different lengths. The resistance of the furnace resistors for a number of intermediate steps is made by connecting two legs in parallel in instances when a low resistance is desired. When a high resistance is wanted the resistors are run in series the current passing through the longest legs only. By properly proportioning the legs, it will be seen that the number of intermediate steps for purpose of regulation may be made as large as desired.

It is, of course, possible to combine these two methods of regulation, namely by voltage and resistance, having a few steps on the transformer and having one or a

<sup>1</sup> Artificial graphite averaging 1/8-inch mesh, but containing no fine powder.

<sup>1</sup> Patented

few resistors capable of being arranged either in series or parallel. A furnace so regulated is shown in plan in Fig. IV and the method is quite suitable for small furnaces of from 4 to 10 sq. ft. hearth area. The construction of the resistor as shown in vertical section would be quite similar to that in Fig. III.

**WIDTH AND DEPTH OF RESISTOR**—This discussion applies to both types of furnaces where the two methods of regulation are employed, *i. e.*, either altering the voltage or the resistance. It has been found that a resistor placed beneath the hearth can be composed of two layers of materials to advantage, the upper of granular graphite and the lower of some material

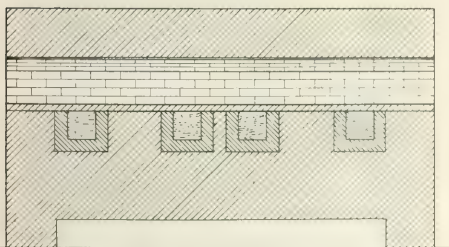
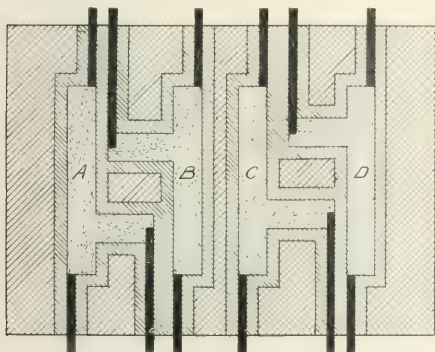


FIG. III FURNACE CAPABLE OF REGULATION WITHOUT A TRANSFORMER—ADAPTED FOR 10 SQ. FT. OR OVER HEARTH AREA

of lower electrical conductivity than graphite, such as charcoal. The lower layer takes a smaller part of the current than does the upper layer of graphite, thus placing the major part of the heat liberated quite near to the top of the resistor. This method seems to protect the part of the lining upon which the resistor rests. It protects it sufficiently well not only to warrant its use, but to make its use absolutely necessary in the case of furnaces operating close to or above 1800° F. A resistor consisting of half charcoal moderately tamped by hand and half graphite gently tamped in is very satisfactory. The resistance of an inch cube consisting in the upper half of granular graphite (pieces  $\frac{3}{32}$  to  $\frac{1}{8}$  in.) and the lower half of hard wood charcoal put in according to the method described above is approximately 0.125 ohm at 1700° F. Thus the area of the cross-section of the resistor may be easily determined after the current necessary has

been computed for the normal running condition of  $1\frac{1}{2}$  volts per inch length of resistor.

**SHAPE OF RESISTOR**—The width and depth of the resistor should be such that as much heat as possible is liberated in the desired direction. For resistors in the hearth this direction is, of course, upward. According to the theory, therefore, the logical shape of resistors of this sort would be as wide as possible and quite shallow. This section, however, is not at all feasible for several reasons. The resistor burns away more rapidly when it is wide and it is more difficult to spread the graphite on a wide resistor when it is replenished. Wide resistors require more lining and the expense of the lining is a relatively important item in the cost. When wide resistors are made to run at right angles the current has a tendency to flow across the interior corner in much higher intensity than at the exterior corner. Sometimes carbon or graphite blocks have been placed in the resistor at the corners for the purpose of reducing this local effect. This, however, is not a very good remedy, as the heat

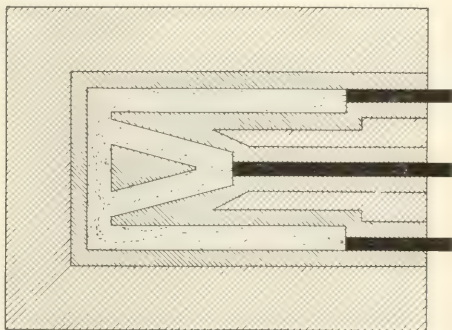


FIG. IV—FURNACE REGULATED BY VOLTAGE AND RESISTANCE SUITABLE FOR 4 TO 10 SQ. FT. HEARTH AREA

liberated in any event is not so great per unit area of the resistor in the corner as in other parts of the furnace. The cross-section of the resistors had, therefore, better be made about square, or wider than the depth by a small amount. If possible the resistors should not be narrower than their depth, but it is impossible to observe this requirement in all cases. Resistors less than  $2\frac{1}{2}$  in. wide should not be used. They should be not less than 6 in. deep and preferably about 7 in., except for resistors over 10 inches wide which can be made 8 in. deep, though more than this is likely to cause excessive heating in the base of the furnace.

**MAXIMUM LIMITATION IN SIZE OF RESISTORS**—The designer frequently has the opportunity of employing one large resistor or two smaller ones to do the same work. Small resistors less than 3 in. wide should be avoided because slight variations in shape have a more marked effect on their resistance than in the case of the large resistors. It is much better as a rule to employ a short resistor 4 or 5 in. wide than a correspondingly longer one  $2\frac{1}{2}$  or 3 in. wide. On the other hand, large resistors are also to be avoided. Since the



thermal conductivity of graphite is rather low it is evident that large resistors are much more likely to become excessively heated in their centers than small ones. Resistors 6 to 9 in. wide are to be used wherever possible, and for resistors of this type 12 inches wide and 8 inches deep are about the maximum dimensions for furnaces used for heating steel. This is quite too large, however, for any heat-treating work, but it is mentioned merely to give an approximation of the maximum limitation of this type of furnace. A 12 by 8 in. resistor would carry 1000 amperes and a number of them could be arranged in a furnace so as to liberate 16 k. w. per sq. ft. of hearth. This is equivalent to a production of about 110 lbs. of steel heated to 1700° F. per hr. per sq. ft. of hearth under the usual conditions. This production is not only more than is usually desired, but is far too much for good work. Experience has shown that a maximum production of about 50 lbs. per hr. per sq. ft. of hearth at 1700° F. is all that can be expected in electric heat-treating furnaces.

**PRODUCTION OF STEEL**—The temperature and the production of steel from an electric furnace are mutually dependent. The heat liberated in the resistor, if not taken up by the metal, will occasion a rise in temperature of the furnace. The larger the electrical capacity per unit area of hearth, the greater the effect on the temperature by alteration in the production. It is for this reason that productions over 50 lbs. per hr. per sq. ft. of hearth should be avoided. With moderate capacities of 4 or 5 k. w. per sq. ft. of hearth area (equivalent to a production of 30 to 35 lbs. of steel per hr. to 1700° F.) variations in production have but very little effect on the temperature. The heat capacity of the resistor lining and brickwork in furnaces of this size is amply able to compensate for changes in production, so that the temperature remains practically the same. A furnace designed for a normal running load of 4 k. w. per sq. ft. of hearth (with 1½ volts per inch length of the resistor) will prove very satisfactory. The uniformity of temperature on the hearth in furnaces employing the T-shaped resistors shown in Fig. III is quite remarkable, but even with the U-shaped or serpentine resistor a temperature variation of less than 10° F., in any point of the hearth from the desired temperature, is to be expected.

**ENAMELING FURNACES** fall quite in the same category with the heat-treating furnaces. Although they are larger in size they are not correspondingly large in electrical capacity. For enameling furnaces resistors should be placed on the sides, but about three-quarters of the kilowatt input should be liberated in the base. Resistors when placed along the sides of a muffle of an enameling furnace should be small, 10 to 20 sq. in. in section and should consist entirely of graphite. The lining of such a resistor is usually designed so as to form a part of the interior wall of the muffle.

#### ELECTRIC FURNACES FOR TEMPERATURES ABOVE 1800° F.

With respect to the class of furnaces operating over 1800° F., the writer knows of no example in industrial work, except on a small scale, which has

proven satisfactory. A number have been constructed and tried for various lengths of time, but a durable furnace, certain of operation, is yet to be produced. Most of the experiments which have been conducted have employed furnaces with a single resistor about half graphite and half charcoal, as mentioned above. These resistors have been made about a foot and a half wide and placed in a trough of a mixture of refractories, the basis of which is firesand. The metal to be heated was placed directly above the resistor, but not touching it. The metal was steel bars for forging and heated to about 2400° F. In order to effect a production similar to that of an oil-fired forge furnace of the same size, the temperature of the resistor had to be above 2900° F. For this temperature it seems impossible to construct a furnace which will have a very long life. In the course of a few weeks the lining or the bricks will have fluxed to some degree and rebuilding will be found necessary. A lining of substantially pure silicon carbide brick might stand up under these conditions, but it is questionable if a refractory any poorer than this would be satisfactory. The electrodes, too, are difficult to hold in place without costly supports which might have to be water-cooled. These furnaces have been used for heating metals for forging and have shown in some instances good economy. A current consumption of 370 k. w. hrs. per 2240 lbs. of metal on a 100 k. w. furnace was noted. In general, the type of construction on these furnaces was similar to that shown in Fig. II, except that the U-shaped resistor was substituted by a single straight one running from one end of the hearth to the other.

For work at forging temperatures a furnace employing a graphite resistor does not seem capable of becoming a commercial reality unless a very unique lining can be developed.

#### ELECTRIC FORGE FURNACE OF THE ARC TYPE

The writer has given considerable thought to this important field of electric furnaces for forging and has developed a furnace which appears to eliminate most of the difficulties encountered. This furnace is as yet only in the experimental stage, although it appears to offer attractive commercial possibilities. It is of the arc type and thus immediately many of the difficulties inherent to the resistor furnace disappear. As there is no resistor there is, of course, no resistor lining. The metal is placed on the hearth and is heated directly by the arcs, the bases of which play a few inches above the metal to be heated, thus obtaining a high thermal efficiency. The arcs are deflected by means of an auxiliary electrode which spreads the flame of the arcs so as to distribute the heat comparatively evenly and also serves to protect the roof of the furnace. The roof, if built of silicon carbide brick, will have a long life. As the electrical equipment is placed above the hearth it is easily accessible and may be removed by a crane so that a new top can be placed on the furnace in a very few minutes. As arcs of a few kilowatts are difficult to operate, it would probably be necessary to build a furnace capable of a very substantial production. The writer hopes

that definite commercial data regarding this furnace can be secured very shortly.

#### DESIGN OF FURNACES FROM STRUCTURAL STANDPOINT

Fig. III shows a heat-treating furnace of 125 k. w. capacity under the normal running load. It has a maximum capacity of 175 k. w. The hearth is 5 ft. wide and 9 ft. long inside.

A very satisfactory furnace wall has been found to consist of two bricks laid so as to make 9 in. and with 3 in. of kieselguhr. The kieselguhr may be placed between the bricks forming a vertical channel, or may be placed outside the bricks, in which case, sheet metal is employed for the outside of the furnace to hold the kieselguhr in place. Asbestos mill board may be used in place of sheet metal. This does not lower the heat losses, and, of course, the mill board is not quite so durable as the sheet metal. Furnaces may be well insulated on the top and sides of the hearth, but care must be observed not to insulate the base too well. It must be recognized that in electric furnaces the heat is evolved within the brickwork and is, consequently, somewhat different from the fuel-fired furnaces. Hence, the furnace should be set clear of the floor with only about 15 in. of brick allowed up to the lining on the base of the resistor. Ten or twelve in. are quite sufficient for this dimension for furnaces working above 1700° F. The brick employed should be good fire brick. Silica brick serve excellently for this purpose. These brick run about 95 per cent silica and contain a little lime. Good masonry work and particularly well constructed arches will be much the cheapest in the long run. Throughout the furnace construction the same principles as are observed in oil furnace design are, of course, applied to electric furnace construction.

**REFRACATORIES FOR LININGS**—It is most important to select the proper refractory for the lining of the resistor. The lining is usually in the shape of a trough, the resistor being placed in it. The lining material must have a high melting point; it must not have a high vapor pressure at its operating temperature; it must not react chemically with the hot resistor on one side or the brick on the other; and it must not become soft or "mushy" at the operating temperature. Its electrical conductivity at the operating temperature must be considerably less than that of the resistor and it must be relatively cheap.

The operating temperature of the lining is rather high, normally a few hundred degrees higher than the hearth temperature, but for various reasons the maximum temperature obtained in a lining may be a thousand or more degrees higher than the normal operating temperature. The reason for obtaining these high temperatures in the lining may be due to neglectful operation or an attempt to get an extraordinarily large production at a particular time. It is, therefore, necessary to employ a lining having a high factor of safety as regards the temperature. It is exceedingly difficult to find a material which meets these requirements at a temperature of 2000° C. (3632° F.). It must be remembered that although refractories of high melting point are available, the addition of the

necessary binder, even though in small amount, may lower the fusing point of the lining very materially. Either of the following substances<sup>1</sup> having high melting points might be employed as the principal constituent of a refractory for use in furnaces operating above 2000° F.

Refractory	Melting point	
	° C.	° F.
Calcium carbide (boils at 2015° C.).....	1995	3623
Aluminum oxide.....	2070	3668
Uranium oxide (U <sub>3</sub> O <sub>8</sub> ).....	2176	3946
Uranium carbide.....	2425	4396
Zirconium oxide.....	2500	4532
Vanadium carbide.....	2750	4982

In addition, two other substances should be mentioned. Glucinum oxide has a high melting point, and boron nitride shows no sign of sintering at 3000° C. (5432° F.).

Magnesium oxide begins to vaporize under atmospheric pressure at 2009° C. (3650° F.). All metallic oxides are somewhat acted upon by hot carbon, and as the speed of reaction approximately doubles for every 10° C. rise in temperature, at electric furnace temperatures this chemical action is often sufficient to deteriorate considerably if not destroy the lining entirely. At about 2000° C. (3632° F.), magnesia is rapidly attacked by carbon.<sup>2</sup>

The electrical conductivity of lining materials, especially metallic oxides, increases very rapidly with the temperature. Materials which are excellent insulators at room temperatures become fine conductors at electric furnace temperatures and this should be borne in mind in connection with the linings. For example, a slab of alundum (fused alumina) had a specific conductivity<sup>3</sup> at 1600° C. (2912° F.) about 50,000 times as great as at 20° C. (68° F.).

In the writer's experience silicon carbide firesand offers advantages over other refractory materials for the linings of furnaces considered in this paper. A mixture of silicon carbide firesand 85 parts, and water glass (38° B.) 15 parts, forms a good lining when well baked in the furnace. A slightly better lining can be made by using the above mixture for the outside of the trough and pure silicon carbide with the water glass in the same proportions for the inside next to the resistor. The lining is put in place with the assistance of wooden forms, and allowed to dry; when the furnace is started it becomes well baked. At operating temperatures such a lining is a much poorer conductor than graphite, and there is practically no chemical action between it and either the carbon or silica brick with which it is in contact. Silicon carbide begins to decompose at about 2300° C. (4172° F.) into carbon and silicon, which vaporizes, but it has given excellent service over a considerable period of time. A silicon carbide lining, properly built in a heat-treating furnace designed to give a hearth temperature of 1850° F., should not need renewal more often than once in six months and frequently such linings last much longer. It will be seen, however, that linings are relatively expensive items in furnace construction so that the firesand is probably the most

<sup>1</sup> "Fusion and Volatilization of Highly Refractory Materials," Ruff and Goecke, *Z. anorg. Chem.*, **24** (1911), 1459.

<sup>2</sup> O. P. Watts, "Action of Carbon on Magnesia," *Trans. Amer. Electrochem. Soc.*, **11** (1907), 279.

<sup>3</sup> E. F. Northrup, *Metal. Chem. Eng.*, **12** (1914), 125.

economical, particularly if 1700° F. is the maximum hearth temperature desired.

The writer begs to suggest that the question of linings for this type of furnace offers an attractive field for research and he sincerely hopes that scientific work along these lines will be made by investigators.

**ELECTRODES** are placed in the furnace imbedded in a mixture consisting of silicon carbide 90 parts, tar (melting point 100° F.) 10 parts. They project from the furnace wall about 6 inches into a box without a top and made of asbestos mill board with a framework of small angles attached to the furnace. The leads are run into the box from the top and are clamped to the electrodes. The box is then filled with kieselguhr. The electrodes may be of either graphite or carbon, preferably the former. The size of the electrodes may be calculated by the well known methods,<sup>1</sup> and either the square or round form may be used.

**SWITCHBOARD**—The switchboard has a main switch, and a radial switch with a number of points, if a transformer is used. The switching may be accomplished on the high tension or the low tension side of the transformer, as is desired. If regulation is effected by altering the resistance with a furnace such as is shown in Fig. III, knife switches alone are used, as no transformer is employed. The resistors are thrown in or cut out by single bladed knife switches, as desired. An ammeter is employed in all cases unless the primary tension is too high to warrant satisfactory operation of same. The ammeter is, of course, always placed on the primary side of the transformer. If an ammeter cannot be used a wattmeter may be employed, or it may be used if an ammeter is not desired by the operator.

**WIRING** should be quite carefully done and with sturdy construction. The chief precaution to observe is to insulate all conductors of current and have such insulation located so that the furnace heat will not injure it. In most cases it is preferable to run the conductors down from the electrodes along or beneath the floor to the switchboard. The switchboard, of course, must be accessible to the operator of the furnace, and is preferably placed by the side of the furnace near the end having the door.

**OPERATION** of an electric furnace of the graphite resistor type is found to be very simple. A new furnace is started up slowly, the voltage equivalent to one volt per inch length of the resistor being applied for about 12 hrs. At the end of this time it may be brought up to temperature by gradually raising the voltage per unit length of the resistor. The metal is passed through the furnaces, the operation being quite the same as in the fuel-fired furnace, and with a very little experience the proper load for each particular job may be readily ascertained. If a change in the production of steel occurs in the furnace, or a change in temperature is desired, it is advisable to raise or lower the kilowatt input, as the case may be,

<sup>1</sup> The writer believes the best method for determining the proper cross-section of electrodes is contained in an article by Carl Hering, "Empirical Laws of Furnace Electrodes," *Trans. Amer. Electrochem. Soc.*, **17** (1910). Table VI in this paper may be employed very satisfactorily for the calculations.

about 15 or 20 minutes before the change occurs. Otherwise, failure to get the production on the one hand, or failure to get the temperature on the other, may be the result.

When the furnace is to be shut down the current may be turned off 15 or 20 minutes before the last piece of metal is removed. The furnace is then closed and as it is quite hot, will take but a short while to heat up after the usual over-night shut down of 14 hrs. The time to heat up after such a period is from 20 to 30 min. To heat the furnace up from cold requires about 1 hr.

**REPLENISHING OF RESISTOR**—As previously stated the resistor burns away partially and must be replenished. This should be done at intervals of about 70 hrs. of operation on furnaces operating from 1700° F. to 1800° F., but furnaces running at lower temperatures will last for longer intervals without replenishing. At 1700° F. hearth temperature the consumption of graphite is approximately 0.01 lb. per k. w. hr. The graphite may be charged through small port-holes, located in the sides of the furnace, by means of long handled scoops. It is then raked down with a small rake adapted to the particular resistor.<sup>1</sup> In some instances the resistor runs uncovered or partly uncovered along the sides of the hearth in the interior of the muffle. In this case the graphite is shoveled in through the furnace door. The proper amount of graphite to be used will be found readily by a few trials, noting the position of the switch before and after charging for the same load.

As the regulation is accomplished by simply throwing the switch, the furnace may be regulated by the workmen. The wiring, of course, must be arranged so that it is impossible to short-circuit the line by means of the switches. The workmen, however, must be instructed not to run the furnace on a voltage equivalent to 1.8 or 2 volts per inch length unless the production really warrants it. Otherwise, overheating may sometimes occur between charges while the furnace is empty. To provide against overheating in this manner, fuses should be carefully selected of low amperage, which is determined by the maximum rate at which the work should be done. This precaution is to be observed particularly on furnaces where productions are varying widely from day to day. For temperatures over 1800° F., it might be advisable to equip the furnace with a pyrometer constructed so as to operate a circuit breaker when the maximum desired temperature is reached.

#### EFFICIENCY

Although the furnace has been designed with the idea of supplying enough current to heat the metal and to make up the losses of radiation, etc., the superintendent of the heat-treating department is very likely to consider the furnace from a standpoint of efficiency. This may be expressed in per cent or kilowatt hours per unit of production. Table II shows the relation between these two methods of expressing efficiency.

<sup>1</sup> The upper surface of the resistor should be raked as level as possible, but it is better to have it slightly concave laterally than convex.



TABLE II—NUMBER OF KILOWATT HOURS REQUIRED TO RAISE ONE TON (2240 LBS.) OF STEEL TO VARIOUS TEMPERATURES AT SEVERAL EFFICIENCIES

Rise in temperature		Percentage efficiency				
° F.	° C.	100	80	70	60	50
Kilowatt hours required						
950	528	89	111	127	148	178
1050	584	103	129	147	172	206
1150	629	118	147	168	196	236
1250	695	134	167	191	223	267
1350	750	150	187	214	249	299
1450	806	164	205	235	274	328
1500	834	171	214	245	286	342
1550	861	178	223	254	297	356
1600	889	188	235	268	313	376
1650	916	197	246	282	328	394
1700	945	207	259	296	345	414
1750	972	217	271	310	362	434
1800	1000	222	278	318	370	443
2350	1306	272	340	388	453	544

In general, the larger the production of metal in a particular furnace, the greater the electrical efficiency. Too high production, however, usually means difficulties in control and with very high production there is danger of overheating should there be slackening in the production without a corresponding change in the kilowatt input being made. The aim to make a production at a rate equivalent to 4 or 5 k. w. per sq. ft. of hearth and also at 65 to 75 per cent efficiency is an excellent one. When the cost of current is rather high, work which necessitates a production at a lower efficiency than 60 per cent should be transferred to a smaller furnace if the shape of the pieces permits. On furnaces under 30 k. w. capacity these figures do not apply, as the efficiency on such small furnaces is very much less than on the moderate size ones of 50 to 125 k. w.

#### INSTALLATION OF FURNACES

In order to determine the number and size of furnaces for an installation a careful inquiry into the nature and quantity of the production is necessary. The maximum and minimum productions must be met with as high efficiency as possible for the various productions. Frequently a moderately large furnace to operate all the time, accompanied by a smaller one to be operated as needed, is much more economical from a point of view of current consumption in the long run, than one furnace capable of the maximum production. Care must be observed not to make the furnace too large for the sake of being on the safe side. A furnace so large that it takes 10 per cent more current than a smaller one exactly suited to the work, would waste enough current in the course of six months, or a year at the outside, to pay for a complete new installation. Sometimes the labor requirements determine the size of the units. Two men on a single furnace might not be able to accomplish so much on the one furnace as they would if operating two smaller size furnaces. Here the decreased efficiency in two furnaces must be carefully compared with the saving in labor.

#### SELECTION OF TYPE OF FURNACE

In the selection of the type of furnace for the particular work, if 10 sq. ft. or more of hearth area are required, a furnace regulated by the resistance method, Fig. III, is certainly to be preferred. This furnace costs about half as much as the furnace equipped with a transformer and has a much more uniform heat liberation in the hearth. Electric furnaces with re-

sistance regulation including all the electrical equipment, cost about the same for installation as a good oil furnace, and frequently are somewhat cheaper if blowing equipment installation charge for the oil furnace is included. As a rule these furnaces operate on a higher voltage than do the furnaces having a special transformer so that a saving in copper for the conductors is sometimes effected. They can be designed to operate on the standard voltages, 220 volts being very satisfactory, and, of course, can operate on either direct or alternating current. The larger furnaces can be built to operate on two- or three-phase lines, but those taking 100 k. w. or less are best constructed for single-phase or direct current. For the small furnaces, such as the one shown in Fig. IV, a regulation by means of voltage is best with a transformer having a secondary with several taps, as mentioned above, either with or without the resistance regulation in conjunction with it.

#### USE OF ELECTRIC FURNACE FOR HEAT TREATMENT DEPENDENT ON COST OF CURRENT

The extent of use of the electric furnace for heat treating depends quite largely on the cost of current. Fortunately, in this connection, the resistance furnaces have a remarkably steady load. The starting load is somewhat less than the running load. In a large number of cases the mean running load is found to be between 80 and 90 per cent of the maximum demand. Under these circumstances, particularly with operation extended into or through the night, current can usually be furnished for a low figure. The price of one cent per k. w. hr. is frequently sufficient to warrant the employment of the electric furnace in place of oil on the ground of cheaper cost of operation alone. Current for three-quarters of a cent per k. w. hr. frequently proves as cheap as any method of firing when all factors are considered. Among these factors, most of which have been duly considered, might be mentioned the lower labor charge which is usually effected by the introduction of the electric furnace. The furnace is conducive to high production on account of the fact that it is not so uncomfortable for the workmen as the fuel-fired furnaces. Besides the fact that it is relatively cool and the elimination of all smoke and dirt, and the attendant difficulties with the products of combustion, the electric furnace is much more satisfactory from the workmen's standpoint than any heretofore produced.

ACKNOWLEDGMENT—The writer wishes to express his appreciation of the assistance of his associate, Mr. Richard S. Bicknell, both in the study and design of these electric furnaces, and in the preparation of this paper.

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#### STUDY OF AUTHENTIC SAMPLES OF GUM TURPENTINE

By A. W. SCHORGER

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#### VARIATION IN PROPERTIES

Turpentine, spirits of turpentine, or oil of turpentine, is the volatile oil obtained ordinarily by the distillation of the oleoresin of various species of pines.

In recent years a considerable amount of "wood turpentine," obtained by steam or destructive distillation of resinous wood has been placed upon the market. To avoid confusion, the turpentine obtained by distillation of the oleoresin or gum is called "gum turpentine."

Gum turpentine consists largely of the terpene  $\alpha$ -pinene, with smaller amounts of camphene<sup>1</sup> and  $\beta$ -pinene.<sup>2</sup> Camphene is not readily affected by light and air, but  $\alpha$ -pinene and  $\beta$ -pinene are soon affected; the specific gravity, index of refraction, and boiling point become higher and there is a pronounced increase in color and non-volatile residue. For this reason the physical properties of gum turpentine will vary considerably, depending upon their age and exposure.

McGill<sup>3</sup> collected 48 samples of turpentine on the open market. After eliminating samples of doubtful purity, he defines turpentine in part as follows: Density 0.860 to 0.880 at 15.5° C., being usually about 0.870; density of the first fraction consisting of 10 per cent by volume, between 0.856 and 0.870, being usually about 0.860. The refractive index should lie between 1.4667 and 1.4722 at 20° C., that of the first fraction should not exceed 1.4700; boiling point between 154° and 158° C.; nine-tenths by volume should distil over below 180° C.

Long<sup>4</sup> found that the specific gravity of pure commercial turpentine varied from 0.8656 to 0.8748. The boiling point was uniformly 155–156° C., and 85 per cent distilled below 163° C.

Veitch<sup>5</sup> and Donk state that a turpentine of standard or No. 1 quality should have a specific gravity of from 0.862 to 0.870 at 20° C.; a refractive index of from 1.468 to 1.476 at 20° C.; and that 95 per cent should distil below 170° C.

Practically all information previously published on the physical properties of gum turpentine is based on the analysis of samples, the age of which is not stated, and consequently it is not apparent to what extent variations existed in the original freshly distilled oils or to what extent they are due to subsequent changes. Although it has been considered that the conditions of production exerted some influence on the quality of turpentine, the extent of such influences had not been determined.

#### VARYING CONDITIONS OF PRODUCTION

The oleoresin obtained by systematic scarification of the trees and caught in appropriate receptacles such as "cups" or "boxes," is known as "dip" among turpentine operators, while that portion of the oleoresin which hardens on the face of the tree is called "scrape." Collectively, the dip and scrape are called "gum."

When the trees are tapped by the box system a cavity called a box is cut into the base of the tree. The face immediately above the box is chipped weekly to produce a flow of gum; as a result, the face is ex-

tended and a height of ten to twelve feet is sometimes attained before the tree is abandoned. The height of the face increases from 18 to 24 inches per year, and the gum must travel a constantly increasing distance to reach the box. The dip collected the first year is called "virgin," the second year "yearling," usually "buck" for the succeeding years. Because of the greater distance the gum must flow during succeeding years, which necessitates longer exposure to light and air; the turpentine has a more or less yellow color and is usually supposed to have a higher specific gravity. The proportion of volatile oil in the oleoresin collected decreases as the height of the face increases and the rosin has a darker color.

The employment of the cup and gutter system or cup and apron system reduces the path, over which the gum must flow, since at the beginning of each season the cup is raised to the top of the face chipped the preceding year. The turpentine obtained from this gum is believed to be more uniform in physical properties and is only slightly colored.

The gum is distilled in ordinary copper-pot stills which hold from ten to thirty-five barrels and are heated directly. A small stream of water is allowed to flow into the still from a funnel in the still head after the greater portion of the water occurring in the gum has passed over. The temperature within the still usually does not exceed 160° C. at the end of the distillation, but when old scrape or dip is being distilled a much higher temperature is often employed. The rosin flowing from one still was observed to have a temperature of 194° C.

The species tapped in the South are almost exclusively the longleaf pine (*Pinus palustris* Mill.) and the Cuban pine (*Pinus heterophylla* Ell.); the shortleaf pine (*Pinus echinata* Mill.), loblolly pine (*Pinus taeda* Linn.), and the pond pine (*Pinus serotina* Mich.) are tapped only casually.

#### COLLECTION OF SAMPLES

The samples which were taken to study the variation in fresh turpentine were collected by the author at the stills and were obtained at various points in the coastal region from Mississippi to Georgia in order that they might be representative of the turpentine produced throughout this belt. They were taken from barrels which were being filled at the still or from those which had just been filled and rolled into the storage shed. Two lots were obtained, one in the fall of 1910 and the other in the spring of 1911. From each of the samples, as complete a history as possible was secured which covered the source of the gum (whether dip or scrape, from boxes or cups, age of the faces, and other similar information) and the part of distillation from which the sample was taken. A summarized description of the samples is given in Tables I and II.

As soon as the samples were collected they were shipped in sealed, 1-gallon tin cans to the Forest Products Laboratory. Analysis of the samples was begun and finished in such time that not more than a month elapsed between the date of collection and analysis.

To determine what variation might be expected in

<sup>1</sup> Schimmel and Company, *Report*, October 1897, p. 68.

<sup>2</sup> *Ibid.*, April, 1908, pp. 99–100.

<sup>3</sup> Inland Revenue Dept., Canada, *Bull.* 79.

<sup>4</sup> *Jour. Anal. and Applied Chem.*, 6 (1892), 2.

<sup>5</sup> *Bur. of Chem.*, Washington, D. C., *Bull.* 135.

large lots of commercial oils, a sample was obtained at monthly intervals from large stock tanks at Pensacola.<sup>1</sup>

For studying the effect of storage, two 1-barrel samples of fresh turpentine were obtained<sup>2</sup> and stored

TABLE I—SPECIFIC GRAVITY, INDEX OF REFRACTION, AND PERCENTAGES DISTILLING UP TO 165° AND 170° OF TURPENTINES COLLECTED IN THE FALL OF 1910

Samp. No.	Kind of gum	Recep- tacle	Year of tapping	Part of run	Sp. gr. at 15° C.	Refrac index at 15° C.	Per cent distillate to
1130	Scrape	Box	1st and 2nd	Last	0.8683	1.4737	92.0 97.5
1131	Scrape	Box	1st	Last	0.8704	1.4743	95.0 97.0
1132	Scrape	Box	4th	All	0.8680	1.4730	95.0 97.0
1133	Dip	Box	1st	First	0.8662	1.4722	97.0 97.5
1134	Dip	Box	4th	First	0.8663	1.4732	94.5 97.5
1135	Dip	Cup	1st and 2nd	First	0.8674	1.4739	91.5 97.0
1146	Dip	Cup	1st and 2nd	Last	0.8673	1.4730	92.0 97.5
1137	Dip	Cup	1st and 2nd	All	0.8683	1.4749	91.0 96.5
1138	Scrape	C & B	2nd	Last	0.8695	1.4744	92.0 96.5
1139	Scrape	Box	2nd	Last	0.8686	1.4737	93.0 96.5
1140	Scrape	Box	5th	Last	0.8678	1.4732	92.5 97.0
1141	Scrape	Cup	1st, 2nd and 5th	Last	0.8681	1.4736	92.0 96.5
1142	Scrape	Cup	2nd	Last	0.8683	1.4729	94.5 97.0
1143	Dip	Box	2nd to 5th	Last	0.8682	1.4735	92.5 96.0
1144	Scrape	Cup	2nd	Middle	0.8667	1.4722	92.0 97.0
1145	Dip	Cup	1st	First	0.8669	1.4732	96.0 97.0
1147	Scrape	Box	1st	First	0.8698	1.4724	96.5 96.5
1148	Dip	Cup	1st	First	0.8659	1.4721	96.5 97.5
1149	Scrape	Box	4th and 5th	Last	0.8682	1.4731	93.0 97.0
1150	Dip	Cup	1st	First	0.8666	1.4724	97.0 97.0
1151	Scrape	Cup	1st	First	0.8674	1.4729	95.5 97.0
1152	Scrape	Box	2nd	All	0.8667	1.4723	95.0 97.0
1153	Scrape	Box	4th	Last	0.8695	1.4735	92.5 95.5
1154	Dip	Cup	1st and 5th	Last	0.8683	1.4732	91.5 97.0
1155	Dip	Box	1st and 2nd	All	0.8674	1.4723	95.5 97.0
1156	Dip	Box	3rd	Last	0.8688	1.4734	92.5 97.0
1157	Dip	Box	1st and 2nd	Middle	0.8671	1.4726	94.5 97.0
1158	Dip	Box	2nd	First	0.8669	1.4732	97.0 97.0
1159	Dip	Box	1st and 5th	First	0.8669	1.4745	89.0 93.0
1162	Scrape	Box	5th	First	0.8669	1.4732	95.0 97.0
1163	Dip	Box	3rd	First	0.8675	1.4737	90.0 96.5
1164	Dip	Cup	1st, 2nd and 3rd	Last	0.8687	1.4750	87.0 95.0
MINIMUM					0.8659	1.4721	87.0 93.0
MAXIMUM					0.8704	1.4750	97.0 97.5
AVERAGE					0.8680	1.4732	93.6 96.7

TABLE II—SPECIFIC GRAVITY, INDEX OF REFRACTION, AND PERCENTAGES DISTILLING UP TO 165° AND 170° OF DIP TURPENTINES COLLECTED IN THE SPRING OF 1911

Kind of Lab. recep- No.	tacle	Year of tapping	Part of run	Sp. gr. at 15° C.	Refrac index at 15° C.	Per cent distillate to 165° or until 5% re- mains	170° or until 5% re- mains
1671	Box	3rd	Last	0.8718	1.4733	90.0	94.5
1672	Box	2nd	First	0.8696	1.4730	90.0	94.5
1673	Cup	2nd	Last	0.8700	1.4745	90.0	94.5
1674	Cup	2nd	First	0.8674	1.4732	92.0	95.0
1676	Cup	1st	All	0.8675	1.4722	95.0	95.0
1677	Cup	1st and 2nd	Middle	0.8704	1.4731	90.5	94.5
1678	Cup	1st	First	0.8678	1.4724	95.0	95.0
1679	Box	7th	Last	0.8703	1.4741	86.0	93.0
1680	Cup	2nd	Last	0.8683	1.4731	92.5	94.5
1681	Box	2nd and 3rd	Last	0.8722	1.4738	87.5	94.0
1682	Box	2nd	First	0.8688	1.4725	93.5	95.0
1683	Box	5th	All	0.8688	1.4724	93.5	94.5
1684	...	...	Whole	0.8691	1.4726	92.5	94.5
1685	Box	2nd to 5th	Last	0.8707	1.4756	89.0	93.5
1686	Box	1st	Last	0.8692	1.4729	94.0	94.5
1687	Box	2nd to 5th	First	0.8694	1.4732		
1688	B & C	2nd to 6th	All	0.8680	1.4722	95.0	95.0
1689	B & C	1st to 6th	Last	0.8678	1.4720	94.5	95.5
1690	B & C	2nd to 6th	Last	0.8678	1.4722	94.5	95.5
1691	Box	1st	Middle	0.8668	1.4714	95.5	95.5
1692	Cup	1st	First	0.8670	1.4714	95.0	95.0
1693	Box	2nd	First	0.8675	1.4717	94.5	95.0
1694	C & B	1st to 5th	First	0.8675	1.4730	91.5	93.5
1695	C & B	1st	Last	0.8668	1.4730	88.0	94.0
1696	Box	7th	Last	0.8719	1.4742	86.0	93.5
1697	Cup	2nd and 3rd	Last	0.8690	1.4745	87.5	94.0
1698	Cup	1st	Middle	0.8678	1.4722	94.5	94.5
1699	Box	2nd and 4th	First	0.8697	1.4740	89.5	93.5
1700	Box	2nd and 4th	Last	0.8713	1.4746	87.0	94.0
1701	Box	2nd	Last	0.8688	1.4744	86.5	93.5
1702	Box	5th	First	0.8680	1.4731	91.5	95.0
1703	Box	4th	All	0.8696	1.4737	90.5	93.0
1704	Box	4th	First	0.8684	1.4734	92.0	94.5
1705	Box	1st and 5th	Last	0.8709	1.4744	92.0	94.0
1706	Box	1st and 5th	Last	0.8671	1.4724	93.0	95.0
MINIMUM				0.8668	1.4714	86.0	93.0
MAXIMUM				0.8722	1.4746	95.5	95.5
AVERAGE				0.8689	1.4730	91.5	94.4

at the laboratory; these were examined at intervals

<sup>1</sup> The American Naval Stores Company, from whom these samples were obtained, state that turpentine is constantly added to and withdrawn from their tanks so that the contents seldom remain undisturbed for a period longer than one week.

<sup>2</sup> From Gillian, Vizard and Company, New Orleans, La.

of four months. The turpentine was distilled from virgin scrape.

#### METHOD OF ANALYSIS

The method of analysis, which consisted of fractional distillation and the determination of the physical properties of the fractions, is fully described in *Forest Service Bulletin 105*.<sup>1</sup> The fractionating apparatus consisted of a twelve-inch Hempel column filled with glass beads. The sample consisted of 500 grams of oil and the fractions collected amounted to approximately 10 per cent except for the first 5 per cent of distillate. For the first lot of samples (Nos. 1130 to 1164, inclusive) about 2 per cent was taken for the first fraction and the distillation was continued until a temperature of 170° was reached or the distillate ceased to pass over. The other samples for which detailed analyses are given (Nos. 1671 to 1705) were distilled in a slightly different manner. The first two fractions amounted to about 2.5 per cent each; the specific gravity of the first fraction was taken separately; then the two fractions were combined and the specific gravity of the mixture was determined. Also it was aimed to leave a residue of 5.0 per cent in the distilling flask. These changes seemed advisable because of the great variations in the properties of the first fraction when it was as small as 1.5 to 2.0 per cent. Furthermore, when either the first fraction or residue is less than 5 per cent, their specific gravities cannot be taken with the Westphal balance in general use in chemical laboratories, and when it is attempted to distil more than 95 per cent of the turpentine, polymerization takes place to a considerable extent; this has the effect of increasing unduly the specific gravity and index of refraction of the residue.

#### ANALYSIS OF FRESHLY DISTILLED OILS

Table I gives the specific gravities, indices of refraction, and percentages distilling to 165° C. and 170° C. for the dip and scrape turpentine collected in the fall of 1910; similar determinations on the turpentines collected in the spring of 1911 are given in Table II. The specific gravity of the turpentines ranged from 0.8659 to 0.8722, with an average of 0.8685 for all conditions of production. The index of refraction of the same samples ranged from 1.4714 to 1.4746, with an average of 1.4730. The specific gravity values are fairly evenly distributed throughout the range indicated, except in the upper portion, where they are more scattered.

**Boiling Point**—The samples collected in the fall of 1910 had a range of boiling point of 155° to 157.6°, the average being 156.1°. The boiling points of the samples collected in the spring of 1911 ranged from 154.1° to 156.0°, the average being 155.8°.

**First Fractions and Residues**—The first fraction amounting to 2.5 per cent had the following properties: specific gravity at 15° 0.8630–0.8655, the average being 0.8645; refractive index 1.4674–1.4708, the average being 1.4691.

The first fraction amounting to 5.0 per cent had the following properties: specific gravity 0.8641–0.8663,

<sup>1</sup> "Wood Turpentines, Their Analysis, Refining, and Composition," by L. F. Hawley.



the average being 0.8652; refractive index 1.4691-1.4710, the average being 1.4698.

As anticipated, the residues showed the greatest variation. The properties of the 5 per cent residues were as follows: specific gravity 0.8873-0.9723, the average being 0.9121; refractive index 1.4837-1.5082, the average being 1.4920.

#### EFFECT OF CONDITIONS OF PRODUCTION ON PROPERTIES

*Season of Year*—The "dip" turpentines collected in the spring had an average specific gravity of 0.8689 while the specific gravity of those collected in the fall was 0.8676. The difference shown by the average values appears fairly consistent in the individual samples, notwithstanding that the lower range is identical for both classes. Of the 35 samples collected in the spring, 19 had a specific gravity higher than the average for all samples, while of the 17 dip turpentines collected in the fall only three fell above the mean value

from first- and second-year faces. The average for all samples of the former class is 0.8691, and of the latter 0.8678. The age of the face seems to have little or no influence on the properties of turpentine distilled from scrape gum.

*Method of Collecting Gum*—The turpentines from boxes have an average specific gravity 0.0012 greater than those from cups, but when individual samples are compared there is little regularity in the values. The average index of refraction and range of refractive values are practically identical for both classes of turpentine.

*Part of Distillation*—The part of the distillation run from which the sample is taken has a very evident influence on its specific gravity. The average gravity of all samples from the first part of the run and of those representing the middle part of the whole run is practically the same, but the samples from the last part

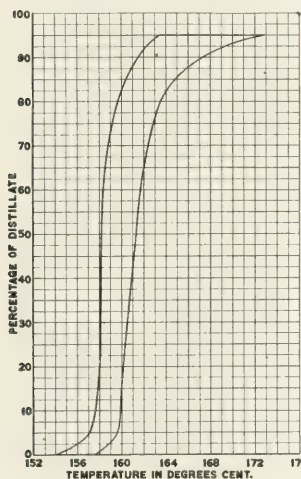


FIG. 1

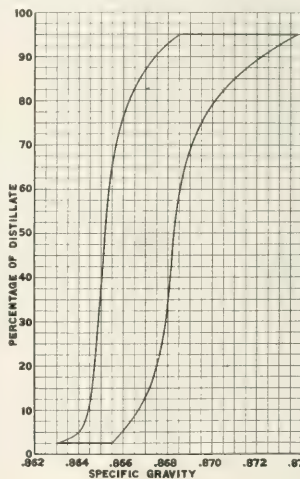


FIG. 2

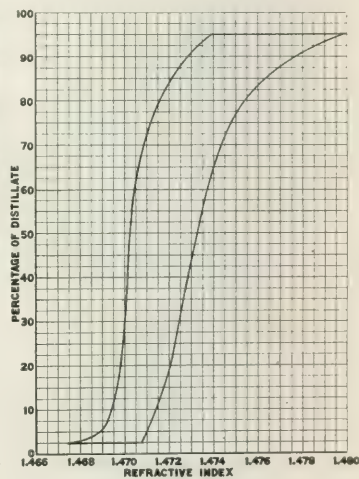


FIG. 3

for all samples. The average index of refraction, as well as the range of refractive values is practically identical for the two classes of turpentines.

*Kind of Gum*—The samples collected in the fall of 1910 included turpentines from both dip and scrape gums. The average specific gravity of the scrape turpentines was 0.8683 and of the dip turpentine 0.8676; the maximum and minimum values were also higher for the scrape turpentines than for the dip turpentines by about the same amount as the average values. The average index of refraction for both classes of turpentines was precisely the same, but the range for the scrape turpentines was a trifle narrower than for the dip turpentines. The average specific gravity of the first fractions and the average values of both the specific gravity and index of refraction of the residues are slightly higher for the scrape than for the gum turpentines.

*Age of Faces*—The dip turpentines from 3- to 7-year faces had a slightly higher specific gravity than those

of the run have higher gravity than those from the first and middle. This variation is fairly consistent among the various classes of samples. The index of refraction of the samples from the last part of the run is also higher.<sup>1</sup>

*Summary*—Turpentines vary in specific gravity with the conditions under which they are produced. The average gravity is higher for scrape than for dip turpentines, higher for turpentines collected in the spring than for those collected in the fall, higher for old faces than for new, higher for boxes than for cups, and higher during the last part of the distillation run than during the first part. These differences are very small; but that they are real and not accidental is in-

<sup>1</sup> The barrel into which the water and oil run from the still and where the separation of water and oil is effected, usually remains from one-half to three-fourths full, the turpentine being gradually dipped out to prevent overflow, consequently the samples are more uniform than it would appear since a sample taken from the last third of the run is not taken from the last third that actually runs from the worm. Furthermore, since the turpentine is distilled in the presence of water vapor there would be no sharp separation into light and heavy fractions.

indicated by the fact that the variations are fairly consistent among individual samples, and that the effects are most pronounced when several factors are combined. The highest average gravity for any group of samples occurs for three which come from the last part of the run on gum collected in the spring from old faces by boxes; the lowest occurs for four samples from the first part of the run on gum collected in the fall from first- and second-year faces, by cups.

The index of refraction varies to some extent for the individual samples, but the average values for the different classes are practically the same.

Although the physical properties of turpentine vary with the conditions of production, the variations are comparatively small and the range of values for normal turpentines is likewise comparatively small. The range for percentage distillation and specific gravity and index of refraction of normal gum turpentines is shown graphically in Figs. 1, 2 and 3. These curves show the extreme limit of physical properties for authentic samples.

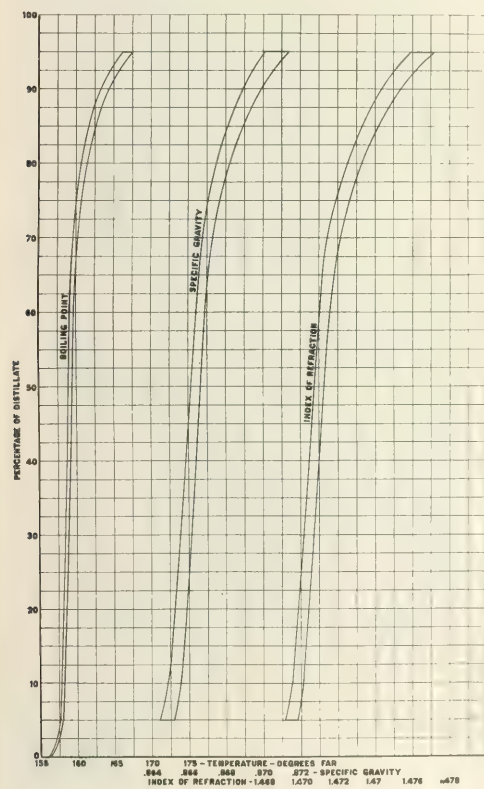


FIG. 4

## ANALYSES OF SAMPLES FROM STOCK TANKS

The analyses obtained at monthly intervals from stock tanks are given in Table III.

The average specific gravity, 0.8689, and refrac-

TABLE III ANALYSES OF TURPENTINES OBTAINED AT MONTHLY INTERVALS FROM STORAGE TANKS

Lab. No.	Date received 1912	Date examined 1912	Sp. gr. at 15° C.	Ind. of ref. at 15° C.	95 per cent distilled up to ° C.
1967	Jan. 8	Jan. 25	0.8696	1.4726	167.5
2216	Feb. 8	Feb. 30	0.8697	1.4726	166.5
2230	March 6	March 8	0.8694	1.4725	166.0
2315	April 8	April 10	0.8694	1.4726	167.5
2115	May 3	May 7	0.8692	1.4726	167.5
2170	June 6	June 10	0.8684	1.4728	167.0
2207	July 8	July 10	0.8685	1.4727	167.0
2417	Aug. 6	Aug. 8	0.8682	1.4727	167.0
2447	Sept. 5	Sept. 10	0.8688	1.4729	167.0
2501	Nov. 4	Nov. 7	0.8687	1.4730	166.5
2546	Nov. 19	Nov. 22	0.8685	1.4730	166.0
2594	Dec. 14	Dec. 17	0.8683	1.4729	166.5

tive index, 1.4727, of these samples agree well with the corresponding average values for the samples examined in the preceding series of tests, namely, 0.8685 and 1.4730. The ranges for percentage distillation, specific gravity, and refractive index for the samples obtained from stock tanks are given in Fig. 4, and are much narrower than those given in Figs. 1, 2 and 3. This greater uniformity is to be expected in the samples taken from bulk quantities. Since it is not known what class of turpentine predominated in a tank at any time, such variations in physical properties as appear cannot be fully explained. However, the higher specific gravity of the samples taken the first months of the year may be accounted for since the first dipping of the season is not distilled until April or May, and scrape turpentines from the previous season would predominate during the winter months.

## EFFECT OF STORAGE

The two barrels of turpentine secured for storage at the Forest Products Laboratory were distilled the middle of December, 1910. Sample No. 1559 was stored in an iron drum, while No. 1560 was left in the original container. Both samples were first examined March 30, 1911, at which time sample No. 1559 was transferred to the iron drum, and were subsequently examined at periods of approximately four months each. The results of examination are given in Tables IV and V.

Sample No. 1559 shows but a slight change after storing for 1½ years, while the specific gravity of

TABLE IV SUCCESSIVE ANALYSES OF TURPENTINE STORED IN IRON DRUM (SAMPLE NO. 1559)

Date of examination	Age Months	Specific gravity at 15° C.	Refractive index at 15° C.
March 30, 1911	3½	0.8685(a)	
July 26, 1911	7½	0.8682	1.4723
December 6, 1911	11½	0.8681	1.4723
April 4, 1912	15½	0.8684	1.4724
August 8, 1912	19½	0.8688	1.4724

No. 1560 has increased but 0.0025 during the same period. The latter sample had to be frequently transferred from one barrel to another because of leakage and was more exposed to the air than the sample in the iron drum which was practically air-tight.

TABLE V SUCCESSIVE ANALYSES OF TURPENTINE STORED IN WOODEN BARREL (SAMPLE NO. 1560)

Date of examination	Age Months	Specific gravity at 15° C.	Refractive index at 15° C.
March 30, 1911	3½	0.8682(a)	
July 26, 1911	7½	0.8680	1.4719
December 6, 1911	11½	0.8681	1.4719
April 4, 1912	15½	0.8691	1.4721
August 8, 1912	19½	0.8715	1.4724

(a) A Westphal balance was used for determining the specific gravities on March 30, 1911, while the succeeding determinations were made with a Gay-Lussac pycnometer to secure greater accuracy. This accounts for the higher specific gravity of the first determinations.

The extent to which sample No. 1559 had changed is shown in Fig. 5, where the distillation data obtained on December 6, 1911, before any appreciable change in specific gravity occurred, are compared with the last distillation made (August 8, 1912). Coincident with the change in specific gravity there is a slight increase in the amount of high boiling constituents and an increase in the index of refraction of these constituents.

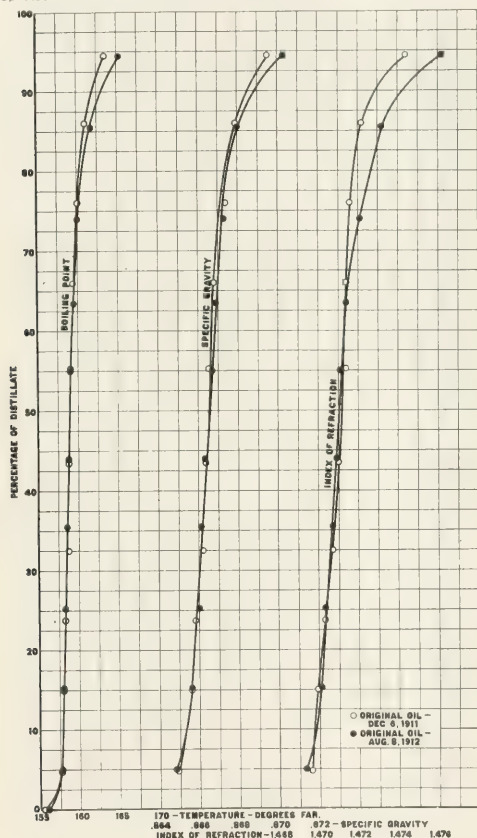


FIG. 5

terpenes. To examine this point further, a three-liter green glass bottle with a narrow neck was filled to within one-half liter of its capacity with turpentine from the same barrel and allowed to stand open to the atmosphere in the laboratory. The average temperature was about 20° Centigrade. The exposure lasted from October 23, 1912, to February 5, 1913, approximately 3½ months. The specific gravity of the oil when set out for exposure was 0.8725 and at

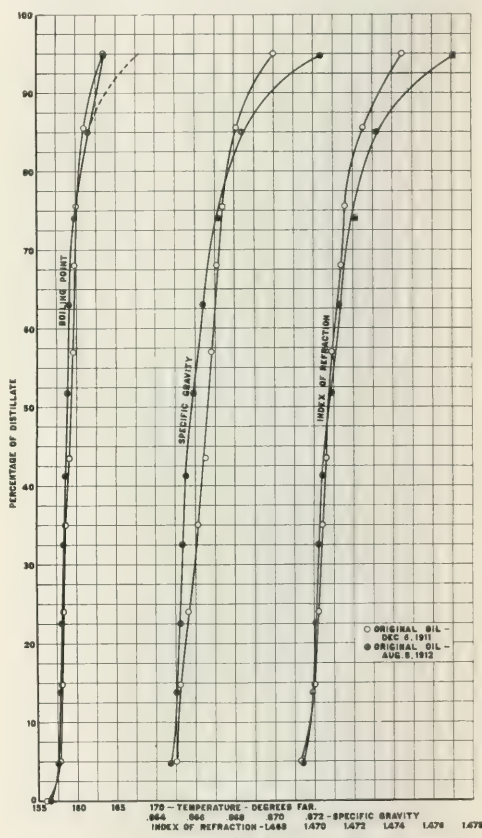


FIG. 6

Fig. 6 shows the change that took place in sample No. 1560 during the same length of time. The original specific gravity had changed 0.0034 and a considerable increase in high boiling constituents was anticipated. It will be noted, moreover, that the boiling point, index of refraction, and specific gravity show a decrease in the lower part of the curves; the difference is especially large for the specific gravity. The boiling point of the last fraction could not be accurately determined, since the mercury continued to drop gradually, although the distillate came over regularly. An explanation that may be offered for the changes occurring in this sample is that a selective oxidation had taken place at the expense of the higher boiling

the end of the test 0.8848, the index of refraction being 1.4746. The curves obtained on distilling 500 grams of the aged oil are compared in Fig. 7 with the curves obtained December 6, 1911. The original oil showed no turbidity and no apparent change in color by aging. The initial boiling point of the oil after exposure was about 145° C., and upon distillation 10 per cent. of water was collected in the first fraction. The amount of water present in the distillate decreased gradually to fraction No. 6—the only clear fraction obtained—and increased from this point to the end of the distillation. In the case of fraction No. 9, the temperature dropped gradually to 135°, the oil distilling regularly until this temperature was



reached, when distillation ceased. Parallel distillations were run and it was found to be impossible to prevent the drop in temperature at this point, even by doubling the rate of distillation. Nearly the full power of the Bunsen burner was required to obtain fraction No. 10, amounting to 1.95 per cent and containing about 10 per cent water. The residue amounted to 12.3 per cent with a refractive index 1.5265 and a

were combined and allowed to stand twelve hours. Considerable water and a yellow sediment deposited. The layer of turpentine was decanted off clear and shaken with anhydrous sodium sulfate and 500 grams were taken for distillation. The results of this distillation are again compared with the original turpentine in Fig. 8. There is a noticeable decrease in boiling point and refractive index, and especially in specific gravity.

From our present knowledge,  $\alpha$ -pinene, camphene, and  $\beta$ -pinene are to be considered the chief terpenes present in gum turpentine.  $\alpha$ -Pinene has a specific gravity of about 0.863 at 15° and boils at 156° Centigrade. Camphene has a specific gravity of about 0.870 and boiling point 160°, but it is one of the most stable of the terpenes towards air and light.  $\beta$ -pinene has a specific gravity of about 0.868 and a boiling point of 164–166°. A greater oxidation of the  $\beta$ -pinene in preference to the  $\alpha$ -pinene would account for the decrease in the values for the physical properties of the fractions.

#### CONCLUSIONS

I—There is a tendency for the specific gravity to be higher for scrape than for dip turpentines, higher for turpentines collected in the spring than for those collected in the fall, higher for old faces than for new, higher for boxes than for cups, and higher for the last part of the run than for the first. However, the differences between the turpentines from these various sources are slight.

II—The properties of bulk quantities composed of turpentines produced under various conditions should

approach the average values given below.

III—Turpentine stored with reasonable care for a period of one year will show little or no change in physical properties.

IV—Aged turpentines will contain varying amounts of oxidation products of the terpenes, depending upon the degree of aging or exposure and should not be considered normal turpentines.

V—The range and average values for the physical properties of normal, freshly-distilled, gum turpen-

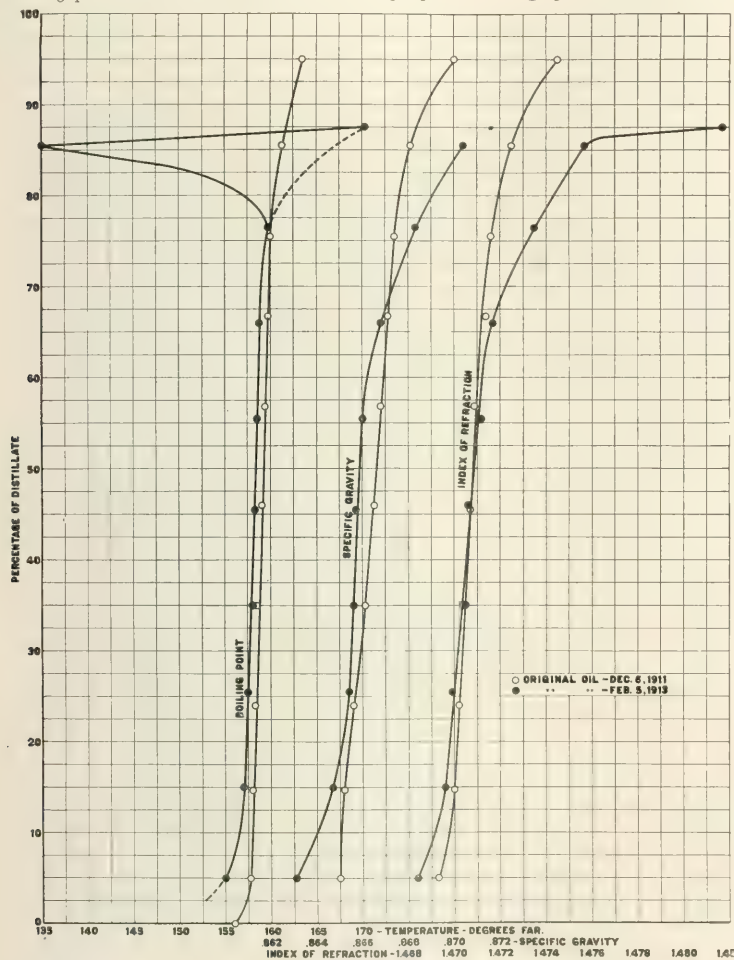


FIG. 7

specific gravity of 0.993 at 25°. The low boiling points of several of the fractions must be due to steam distillation caused by the presence of water. The water doubtless results from the breaking up, on heating, of the hydrates formed by aging.

Owing to the presence of water, the distillation of the oil altered by age did not give satisfactory information in regard to the changes which may have taken place in certain of the constituents. Accordingly, the first nine fractions of the two parallel distillations

tines, based on the analysis of 67 samples, are as follows:

1—The specific gravity at 15° C. will fall between 0.8659 and 0.8722, with an average of 0.8685. The index of refraction at 15° C. will fall between 1.4714 and 1.4746, with an average of 1.4730. The initial boiling point will not be lower than 154° or higher than 157.6°, and will average about 156°.

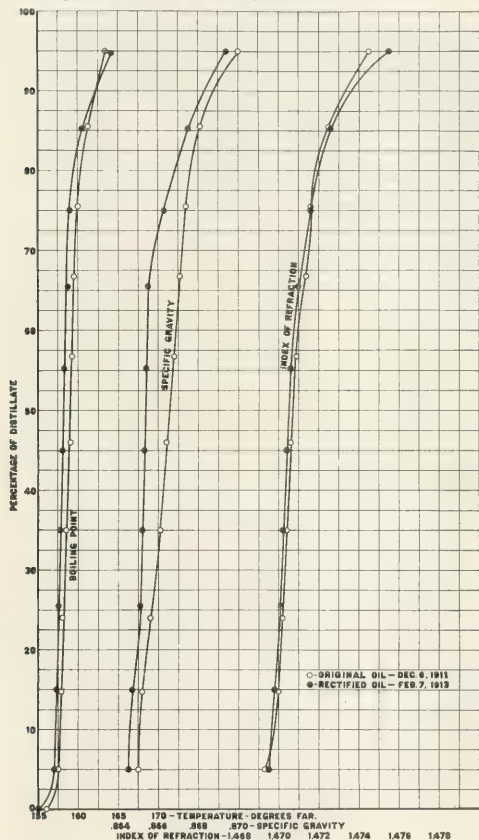


FIG. 8

2—The first fraction by the method of distillation used, amounting to 2.5 per cent, will have a specific gravity not lower than 0.8630, and will average about 0.8640; the index of refraction will be not lower than 1.4675 and will average about 1.4690. If the first fraction amounts to 5 per cent, the specific gravity will be not lower than 0.8640, with an average of 0.8650; the index of refraction will be not lower than 1.4690, with an average of 1.4700.

3—At least 86 per cent, generally 91-93 per cent, will distil up to 165°; and at least 93 per cent, generally 97 per cent, will distil up to 170°.

4—The residue of 5 per cent will have a specific gravity not lower than 0.8875 and it will average about 0.9140. The last fractions should show a steady

increase in specific gravity. In no case should the specific gravity of any fraction be lower than that of the previous fraction.

FOREST PRODUCTS LABORATORY  
FOREST SERVICE, U. S. DEPARTMENT OF AGRICULTURE  
(In Cooperation with the University of Wisconsin)  
MADISON

## THE HYPOCHLORITE OF LIME TREATMENT OF A MUNICIPAL WATER SUPPLY AND A STUDY OF CERTAIN RESISTANT BACTERIA

By STANLEY JESSEN THOMAS

Received April 9, 1914

### INTRODUCTION AND HISTORY

On March 27, 1909, the Council of the City of Bethlehem, Pa., passed an ordinance appointing a committee to investigate conditions and decide upon a site for a new water supply for the city. This was the first official act taken that contradicted the idea that Bethlehem was being supplied with pure water. Until a few months previous the city was supposed to have one of the best water supplies in the State of Pennsylvania. While the cistern has been more or less in vogue in this community always, yet as a municipality Bethlehem may be said to have probably the oldest public water system in the United States. The old pumping station back of the Eagle Hotel is an historic landmark, ranking in age with the Moravian Chapel and some of the rest of the city's pre-Revolutionary buildings. When one considers the length of time that this source has supplied the city with water, it can readily be seen how some of the citizens objected to a seemingly enormous outlay of money for a new supply.

On July the fourteenth, 1909, Council authorized the purchase of Illick's Mill site and gave permission to the committee to spend the necessary money for drilling wells. A bond issue was then placed before the people and in the fall of that year it was passed. There were objections raised, however, and the case was taken to the Supreme Court. The Court decided that the ballot had been defective and that the bond issue was defeated. Work on the Illick's Mill plant was necessarily suspended and Bethlehem saw no chance for a change in water supply.

The city had grown enormously in the last decade in the vicinity of the old spring and it was well known that the water was badly contaminated. The spring and well were down in a hollow surrounded by buildings. Theoretically, one could not look for a worse place from which to draw a public water supply. Practically, the water was being polluted as badly as could be conceived of.

It might be well to state here just what constitutes a "good" water supply and wherein the Bethlehem water failed to fulfill the requirements. Savage (Savage—Water Supplies, page 2) classifies bacteria found in water into three divisions.

1—Normal inhabitants, as *B. fluorescens liquifaciens*. This class comprises all bacteria which find water a suitable medium for their growth and multiplication. This class may be present in large numbers without necessarily indicating contamination. It would mean,

merely, that an abundance of food in the shape of organic matter was present. This organic matter may be objectionable or not as chemical analysis would show.

2—Unobjectionable aliens, as *B. mycoides*, which are washed in from pure soil. This class in itself is not objectionable, but its presence shows the advisability of watching the water for,

3—Objectionable aliens, or bacteria gaining access to water from polluted sources as sewage or animal excreta. This class is directly indicative of danger and the greater their number the more immediate and massive the dangerous contamination.

Thresh (Thresh, 1903) in August, 1903, described an epidemic of diarrhea due to the use of impure water. There were 1000 cases and 14 deaths. The outbreak was due to heavy rains sweeping washings from the adjacent soil into a small reservoir into which the public water flowed. The soil around consisted of garden ground manured from time to time with road sweepings. The water supply itself, apart from this local pollution, was an uncontaminated one.

Now deep well water or spring water is water which, whether initially pure or impure, has filtered through a considerable depth of soil and rock. Soil at the depth of 8–10 feet is practically germ-free while it also acts as an efficient filter. Soil, therefore, while adding nothing to the water but rather filtering off the bacteria should cause deep well water to be quite free from germs. Hence, Class I should be present only in small numbers and the presence of Class III even in very small numbers should be sufficient to condemn it.

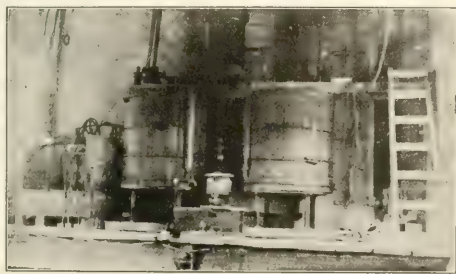
As we know, the Bethlehem water was taken from a deep well and spring. The total count of Class I ran up sometimes as high as 200,000 per cc. This alone should condemn it, but to this is added the fact that Class III (*B. coli*) was present in numbers as high as 1000–10,000 per cc. The former result might be excused in a mountain stream but not in a well supply. The presence of *B. coli* in numbers greater than 1 to the cc. should condemn any water. In other words, Bethlehem was drinking diluted sewage for some time before the danger became apparent and could not go on taking her water from this source. As the proposition to change the source of supply was lost, there remained only one thing to do, namely, to treat the water with some germicide to destroy the bacteria and so make it suitable for drinking purposes.

Several methods of purification were suggested: (1) the copper sulfate method used in Scranton at the time of their epidemic in 1906–1907, (2) the alum sedimentation treatment, (3) the copper treatment, and (4) the hypochlorite of lime disinfection. The last named depends on the fact that hypochlorite of lime when acted upon by organic matter liberates oxygen which destroys almost every known germ. It is certain that this treatment kills all disease germs. It was this treatment that was chosen for the Bethlehem supply.

Treatment was started in the summer of 1911 and did satisfactory duty as far as purifying the water was concerned until the Illick's Mill pump was permanently started in November, 1912.

From the time of the Supreme Court decision in 1909 until September, 1911, nothing was done officially about the purchase of a new water site. On September the twenty-fifth, 1911, Council passed a new ordinance granting \$175,000 for "The purchase and maintenance of an adequate water system at Illick's Mill," but this ordinance was vetoed by the Burgess. On March twenty-fifth, 1912, however, Council granted \$50,000 for the same purpose and passed the measure over the Burgess' veto. From then on the work has been progressing rapidly and water was finally pumped into the city mains in November of 1912. The Illick Mill station is now furnishing Bethlehem with a good supply of pure water.

At the time of the installation of the "Hypochlorite" plant the water from the old source showed fearful contamination. Immediately after it was started the



VIEW OF THE HYPOCHLORITE PLANT USED AT BETHLEHEM, PA.

number of bacteria dropped and with the perfection of the plant they were soon entirely eliminated. There is no doubt that at the early stages of its use, more hypochlorite was put into the water at times than was necessary, but this error was on the side of safety, and was overcome with experience in handling and the perfection of a mechanical method of adding the hypochlorite. The efficiency of the hypochlorite as an antiseptic may be seen by an examination of the following tables and charts. The primary source of the old supply was a spring; as this was found to be insufficient a well was sunk near-by and the water from it pumped into the spring basin. This was the "raw water" and was pumped from here through the hypochlorite plant into the mains. The "pump" water was taken from a tap at the pumping station immediately after it had passed through the treatment, and the tap water was taken from a tap some distance from the station. An idea of how the bacterial count of the water varied and the result of the treatment may be gathered from the following, Table I showing results of consecutive analyses.

A glance at Table I will show two things plainly: 1—That the water was comparatively good from the bacteriological standpoint one day and very bad the next, often jumping from about 5,000 bacteria per cc. to 100,000 per cc. and then back again to 5,000 on the next analysis; 2—That this rapid rise in numbers did not follow any regular sequence of events as would result if the rise were caused by rains, etc. As a mat-



DATE	TABLE I					
	RAW WATER		PUMP		TAP	
	B. Coli	Total count	B. Coli	Total count	B. Coli	Total count
Feb. 1.....	80	51000	0	4	152	
3.....	150	37000	0	3	21	
5.....	60	162000	0	3	750	
7.....	500	15000	0	0	90	
9.....	90	55000	0	2	520	
Oct. 16.....	10	1800	0	0	0	
18.....	1000	23000	0	10	0	45
20.....	10	27500	0	0	0	1
24.....	0	17500	0	2	0	450
26.....	0	100000	0	1	0	400
28.....	90	18500	0	2	0	60

ter of fact, the lowest results were obtained after heavy rains, showing that the surface washings around the spring were diluting the water in its bacterial content rather than adding to it.

Table II shows the resistance of *Micrococcus agilis*, *B. subtilis* and *Bact. aerophilum* to the hypo-

TABLE II—HYPOCHLORITE OF LIME						
Parts per million.....	0.1	0.5	1	1.5	2.0	Blank
<i>Bacillus subtilis</i> .....	80,000	4600	710	20	1	500,000
<i>Micrococcus agilis</i> .....	6,000	2000	100	1	1	1,600,000
<i>Bacterium aerophilum</i> .....	10,000	2100	200	30	5	400,000
<i>Sarcina lutea</i> .....	7,000	10	0	0	0	800,000
<i>Bacillus aurantiacus</i> .....	5,000	0	0	0	0	1,000,000

chlorite of the lime treatment. Table III shows the resistance of the same germs to other germicides. In each case the bacteria were introduced in the vegetative stage and the culture allowed to stand 3-5 days plating.

Unfortunately, the blank tests did not give the same number of bacteria introduced in every case but they are near enough for comparison. The other two bacteria used (*Bacillus aurantiacus* and *Sarcina lutea*) are non-

Parts used	Formalin			Mercuric chlorid			Phenol			Blank
	1-10000	1-1000	1-100	1-25000	1-10000	1-5000	1-200	1-100	1-20	
<i>Micrococcus agilis</i> .....	30	0	0	10	0	0	20	0	0	400,000
<i>Bacillus subtilis</i> .....	2000	0	0	110	0	0	300	0	0	800,000
<i>Bacterium aerophilum</i> .....	240	25	0	1500	900	0	9000	300	0	5,000,000
<i>Sarcina lutea</i> .....	10	0	0	0	0	0	0	0	0	900,000
<i>Bacillus aurantiacus</i> .....	40	0	0	0	0	0	0	0	0	400,000

spore forming germs while *Bacterium aerophilum* shows the greatest resistance in each case. I think their lack of motility aids them somewhat in clumping and so not being so readily attacked by the germicides.

On examining the gelatin plates after forty-eight hours incubation, various small colonies were found from time to time. It was noticed that on an examination of the water on a particular day, the "pump" analysis showed no bacteria at all while the "tap" analysis showed a great number per cc. The fact brought up the question as to the cause for their presence. Of course the untreated water showed an enormous variety of forms, but why should the treated tap water show colonies time after time when the samples taken shortly after treatment at the pump were practically sterile? This may be explained in two ways. First, that small clumps of organic matter passed through the pump without being penetrated by the hypochlorite of lime, or second, that there are some forms which are able to resist to some extent the hypochlorite treatment. As a matter of fact, both of these suppositions are true.

From numerous analyses I collected from ten to fifteen different forms of bacteria. I then treated them with approximately the same strength of hypochlorite of lime as we were using at the pumping sta-

tion. About six forms resisted this treatment, showing that the presence of the rest was simply due to their accidentally escaping treatment in passing through the plant in clumps of organic matter. After repeated trials I eliminated two more forms and so had four bacteria that I knew could resist the hypochlorite treatment of the strength of two parts per million.

Before going any further with the resistance of these germs, I identified them as *Bacillus subtilis*, *Micrococcus agilis*, *Bacterium aerophilum* and *Bacillus cuticularis*. Below are given the results of my study of each of these germs:

#### BACTERIUM AEROPHILUM

*Bacterium aerophilum* (Flügge), *Bacillus aerophilus* (Migula).—*Bacterium aerophilum* grown in bouillon for forty-eight hours at 20° shows extremely sluggish motility and can really be called a non-motile rod. The rods are very slender but of various lengths, ranging from 1.5  $\mu$ . to 3.5  $\mu$ . The rods often hang together in short straight chains or threads, but very seldom have a capsule. A destined line of demarcation can be seen between any two rods in a chain. Oval glistening spores may be demonstrated after twenty-four hours growth on agar at 37.5° C. The spores are equatorial and the rods are not swollen at sporulation. No vacuoles could be shown in *Bacterium aerophilum* nor can flagella be demonstrated. Pleomorphism is shown in the varying lengths of the rods. The bacterium stains readily with aqueous stains or carbol fuchsin. Gram's stain is negative.

*Bacterium aerophilum* forms no gas or acid in dextrose broth. In bouillon no membrane forms on the surface and while the broth is slightly cloudy no deposit is thrown down.

On gelatin plate cultures it forms after forty-eight hours at 20° very small, fine, punctiform colonies. After 72 hours these colonies are slightly larger, round or pear shaped, with a greenish yellow color and entire edges. After about four or five days, liquefaction begins and while the liquefaction is very rapid after it once begins there is very slight growth in the colony itself.

On the gelatin stab, liquefaction begins only after four to five days and then there seems to be no growth along the needle track except at the surface. The liquefaction is always saccate, showing that the bacterium is strongly aerobic. The upper part of the liquefaction is yellowish green and appears uniform while the lower part is opaque and flaky. There is no odor.

On agar *Bact. aerophilum* forms a thick wrinkled growth.

On potato it forms a yellowish growth with a smooth surface of a dull, paraffin-like appearance. Later the surface dries at the edges, taking a granular appearance; after a week the whole surface becomes wrinkled.

On litmus milk no acid is formed nor is the milk coagulated. There is no indol production. It does not reduce nitrates. *Bacterium aerophilum* is non-pathogenic. It is strongly aerobic, and is widely distributed in air and water.

#### MICROCOCCUS AGILIS

*Micrococcus agilis* or *planococci agilis* (Migula) generally occurs in the form of single cells, diplococci or tetrads which are clumped together in irregular masses. On cultivation in broth, however, at 20°, for forty-eight hours, typical sarcina pockets of eight to sixty-four cells can be shown on the hanging drop slide. The cells are oval, being slightly longer than they are broad, being in their longer diameter 0.8  $\mu$  to 1  $\mu$ . Motility is rather rapid after growth in favorable culture media. Flagella must be present because of the motility but I was unable to demonstrate them. Migula says: "The flagella of *Micrococci agilis* are very hard to stain, generally only a part of the lash taking the stain. Usually only one flagellum can be demonstrated to a cell, sometimes two can be shown, but rarely more. The flagella are very long—about ten times the length of the cell and irregularly situated." No spores could be shown. The capsule is very thick and resistant to stains. *Micrococcus agilis* takes aniline stains, however, by gentle heating and retains them even when washed with alcohol. Gram's stain is positive.

*Micrococcus agilis* forms no gas or acid in lactose or dextrose bouillon. A slight cloudiness develops but no scum or sediment appears. There is no production of indol, nor have the bacteria any action on nitrates.

On gelatin plates for five or six days the colonies were small, grayish white specks which after this time assumed a pinkish color. The deep colonies remain small and are a grayish red color while the surface colonies become bright rose colored specks. The former appear under the microscope as entire round homogeneous spots rather highly refractile. The surface colonies are also entire discs but somewhat larger. From about the sixth day slight liquefaction of the gelatin starts which proceeds very slowly, evaporation always exceeding liquefaction.

The gelatin stab showed a faint white streak along the needle path which spreads out at the surface in a white raised growth. After six days at 20° the colony slowly sinks into the gelatin in a pink dry funnel. There is no odor at any time.

On slant agar the streak is beaded, becoming echinulate with white edges with a pink color in the deepest center. The streaks grow very slowly with a slight smooth elevation.

On potato the growth of *M. agilis* is rather rapid, pink sheets appearing after 72 hours at 20° which spread over the entire surface. The color gradually darkens with the media. Litmus milk does not coagulate. The best temperature is about 20°, the bacteria not growing well much below that temperature and not growing at all at 37.5°.

The micrococcus was first isolated from water by Cohn.

#### BACILLUS SUBCUTICULARIS

*Bacillus subcuticularis albus* (Tataroff)—Grown in broth for forty-eight hours at 20° C., the bacillus is actively motile. It usually forms double rods and appears like a long rod which is bound in the middle. It has rounded ends and is about 3.2  $\mu$  long. On agar it forms chains which are of various lengths and mostly motile. Sometimes the chains appear to wiggle like worms. Most of the chains have spores.

Gelatin colonies show peculiar characteristics. On the plate culture the surface colonies appear as bluish white shining specks; under the microscope they appear brownish, granular, and of irregular contour. The edges are very irregular. The deeper colonies are entire, of irregular shape and brownish. After 3–4 days they are berry shaped, with a solid brown spot surrounded by granular grayish specks.

On the gelatin stab the surface growth is irregular, bluish white, becoming brownish. It is rosette shaped and very glistening. It appears as though it were of several layers, one overlapping the others. Along the needle path are several small beads, which show after 3–5 days a growth similar to the deep colonies on the gelatin plate. It is at first white and round. Later, after 3 days, a number of wart-like forms appear on the surface. After 5 days the colony is covered with these warts and is rosette shaped. The colony now appears like a white ball around which is a cord wound in all directions. The background is much lighter than the ribs around it. After a week the gelatin becomes softened and the colony itself appears gluey.

On agar slant the growth is white, glistening and spreading. Old cultures appear grayish and are lapping.

In bouillon a white pellicle forms on the surface, the medium becomes cloudy and after 3–4 days at 20° a flocculent precipitate is thrown down.

On potato the growth is very rapid, covering the medium in three days at 20°. The surface is irregular and lapping, of a brownish color.

*B. cuticularis* stains readily with ordinary stains, but is negative to Gram's stain.

It is aerobic and non-pathogenic.

#### BACILLUS SUBTILIS

*Vibrio subtilis* (Ehrenberg).

*B. subtilis* (Cohn).

*B. subtilis* grown in bouillon for forty-eight hours at 20° or for twenty-four hours at 37.5°, proves to be a very actively motile straight rod form. The rods vary from short thick ones to long chains of long ones. The long chains showed sluggish motility. The shorter rods were 0.8  $\mu$  to 1  $\mu$  in thickness and about 2  $\mu$  in length. Some were about 1.3  $\mu$  in thickness and 5  $\mu$  in length. The ends of the rods were squarish. No spores could be found at this incubation, but on a slant agar growth of twenty-four hours at 37.5° they may easily be demonstrated. The spores are equatorial and the rods are not swollen at sporulation. When the spores begin to form the plasma of the cell becomes granular and a weakly refractile round body forms in the center. This grad-

ually becomes more strongly refractile until finally the definite shape of the spore is reached. The spore is surrounded by a thick membrane while the capsule of the mother cell weakens. The spore formation is most noticeable in the threads. On germinating, the spore gradually takes an elliptical shape, the refractile properties lessen and the spore swells until it breaks at the ends and the young rod is formed. At first the rod is not motile but it soon becomes so. The motility continues only a short time but the rods will stay together in longer or shorter threads which are immotile. *B. subtilis* possesses vacuoles and granular bodies, especially when the rods form in chains and begin to sporulate. The bacillus possesses a capsule and flagella which are long and numerous, being peritrichic. Pleomorphism in *B. subtilis* is very striking, rods taken from the same media varying from  $2\mu$  to  $5\mu$  in length. The bacillus stains readily and uniformly by carbol-fuchsin and methylene blue. Gram's method gives a positive stain.

*Bacillus subtilis* forms no gas in dextrose broth or lactose broth. Bouillon tubes show opacity after twelve hours incubation at  $37.5^\circ$ . After twenty-four hours a thick-wrinkled, white pellicle forms on the surface of the bouillon, a deposit forming in the bottom of the tube shortly afterward. The bouillon was alkaline. No indol production takes place in dextrose-free bouillon.

On gelatin plates crateriform colonies of rapid growth soon liquefy the plate if grown very much above  $20^\circ$ . At  $18^\circ$ – $20^\circ$ , however, while liquefaction can be seen, the colonies, unless numerous, do not spread greatly. The colonies are nearly circular. Microscopically the colonies are round and entire, although after 2–4 days, when liquefaction is decided, the edges of the colonies are ciliated and the colonies themselves become dense and floccose (a thick grayish white mass in the center joined to the edge of the colony by light gray threads). On agar plates colonies are small and irregular. Microscopically they look like wreaths with small branches sticking out at the surface.

Gelatin stab shows at first a white thread along the needle path from which fine threads shoot out into the gelatin. In a short time, 8–10 hours at  $20^\circ$ , the liquefaction becomes crateriform, which gradually becomes saccate and then tratiform, always holding a thick scum of pores on the surface of the liquefaction.

On the agar slant the growth is moist and glistening, filiform becoming crumpled and soon spreading over the entire surface of the agar. The center of the stroke is lightly raised. On potato the growth is very rapid, white, thin and moist-looking. The growth very rapidly spreads over the whole surface of the potato. *B. subtilis* quickly coagulates milk without the formation of acid. *B. subtilis* is a non-pathogenic bacterium, aerobic or facultative anaerobic which grows most rapidly at  $37.5^\circ$ . It is very widely distributed in nature, and may easily be isolated from water or vegetable growth.

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## THE RADIOACTIVITY OF THE WATERS OF SARATOGA SPRINGS, NEW YORK<sup>1</sup>

By RICHARD B. MOORE AND C. F. WHITEMORE

Received June 9, 1914

At the request of the Commissioners of the State Reservation at Saratoga Springs, New York, to the Director of the Bureau of Mines, an examination of some of these waters was made by the authors with a view to determining to what extent the waters and the gases evolved from them were radioactive. The work done involved the direct testing of the gases evolved from the springs for thorium and radium emanation; the examination of the waters: (a) for their total activity; (b) of a certain number for the activity due to dissolved radium salts; and the determination of the activity of the residues deposited by the springs, where such residues could be obtained.

The springs tested were selected from the three main groups which are found at Saratoga, namely, High Rock Park, Congress Park, and Geyser Park. High Rock Park is at the northern end and Congress Park is in the center of the town. In the former group, among others, are included the Peerless and New Red springs, while the principal spring at Congress Park is Hathorn No. 1. Several springs were also examined in Geyser Park which is two miles to the southwest of the town. In this group are included the Coesa Spring, Hathorn No. 2, Hathorn No. 3, and others. One spring, the Crystal Rock, not belonging to the State Reservation is included in the list. This spring is situated several miles to the north of Saratoga.

The activity of any water may be due to the presence of (a) dissolved thorium or radium emanations, (b) dissolved thorium and radium salts. All mineral and deep well waters are more or less radioactive, but the activity is usually due to the presence of dissolved radium emanation, not to dissolved radium salts. Therefore, the fact that a water is radioactive has of itself little significance. What must be determined is how active the water is and what proportion of this activity is due to dissolved emanation and what proportion to dissolved salts.

Tests on the activity of the evolved gases were made on the ground in the following manner: A glass funnel to which was attached a rubber tube connecting with a small rubber bulb in turn connected with one of the openings to an electroscope, was inverted over the spring at a point where the evolution of gas was greatest. By pressing the bulb, a continuous and fairly constant supply of the gases from the spring was passed through the electroscope. By stopping the flow of gas and immediately making a series of readings across the scale, each reading being of short duration, it was possible to ascertain whether the activity was entirely due to the presence of radium emanation. If thorium emanation was present a very sudden drop in activity would be noticed and, after a few minutes, the curve obtained by plotting activity against time would flatten out, due to the decay of the thorium emanation. In no case was thorium emanation found in any of the

<sup>1</sup> Published by permission of the Director of the Bureau of Mines.



gases evolved from the springs, the activity being entirely due to the presence of radium emanation.

In order to obtain a quantitative result on the latter, a definite volume of the gas was collected in an inverted graduated bottle. After noting the volume, the temperature and pressure, this gas was introduced into the electroscope and readings at once made. The necessary correction for the increase in activity obtained at the end of three hours was made as it was not possible under field conditions to wait for this maximum activity to be attained.

In order to get the activity of the waters, samples were collected at the springs at a point nearest to the source of supply. The bottles were hermetically sealed and shipped to the laboratory in Washington by express. They were then boiled in the apparatus designed by Schlundt and Moore<sup>1</sup> and the evolved gases containing the radium emanation were introduced into a standardized electroscope. On account of the large amount of carbon dioxide contained in some of the waters it was found advisable to add a sufficient amount of c. p. sodium hydroxide before boiling. In order to differentiate between the activity due to radium salts in solution and that due to dissolved emanation, samples of some of the waters were treated with c. p. hydrochloric acid, boiled for fifteen minutes and then sealed in flasks and allowed to stand for a month. At the end of this period they were boiled in the usual way and from the activity obtained it was possible to calculate the amount of radium salts in solution.

Samples of the deposits from some of the springs were also collected and fused with sodium carbonate according to the method of Strutt.<sup>2</sup>

Column 2 in the table of results gives the activity per liter at standard temperature and pressure, of the gases evolved by the springs; Column 3 gives the total activity per liter of the water, and Column 4 the activity per liter of the water due to dissolved radium. Column 5 shows the activity of the material deposited either in or just around the outlet of the spring.

SPRING	Temperature ° C.	GAS Radium per liter $\times 10^{-11}$	WATER Radium per liter Gram $\times 10^{-11}$		DEPOSIT Radium per gram Gram $\times 10^{-11}$
			3	4	
Emperor.....	9.7	22.1	7.0	6.8	
Peerless.....			6.0		
New red.....	10.0	8.0	4.3		
Hathorn No. 1.....	10.2	21.3	14.2	4.2	76.9
Coesa.....	10.2	8.1	9.7		7.9
Hathorn No. 2.....	10.0	5.1	16.1	-9.9	
Hathorn No. 3.....	9.5	8.3	6.6		12.0
Geyser.....	9.7	3.4	3.9		1.7
Adams.....	11.0	11.7	12.2	5.1	8.8
Flat No. 2.....	10.5	3.7	5.0		6.5
Pump well No. 4.....	12.0	67.8	23.1	2.1	6.3
Island.....			11.8		10.5
Crystal rock.....	10.0	84.7	88.0	0.9	
New shotts well.....			11.3		

Although there is a fair agreement between the activities of the gases and waters, this agreement is not exact, nor is such to be expected as the activity per liter of any gas will be largely influenced by the rate of flow of the gas, which varies with the different springs and has not yet been measured. A similar statement can be applied to the results in Column 5. The activity of the deposits per gram will depend not only

on the amount of radium precipitated from solution, but also upon the quantity of other material precipitated at the same time. The fact that the residues are radioactive shows that the waters contain dissolved radium salts in addition to dissolved emanation, but this fact is more precisely indicated by the results under Column 4.

The activity of the gases is not high, a result to be expected owing to the fact that the flow of gas in the majority of the springs is quite large.

The total activity of the waters is rather low, although that of the Crystal Rock spring is considerably above the average. The activity of this spring, however, is not exceptional. A very large proportion of the activity due to dissolved radium salts, as shown in Column 4, is, however, quite exceptional and as this statement applies to all of the springs under Column 4, with the exception of the Crystal Rock, it is reasonable to suppose that it probably also applies to those not examined for dissolved radium salts.

Many of these springs contain considerable amounts of barium bicarbonate, as has been shown by analyses made by the State Department of Health of New York, Hathorn No. 2 carrying as much as 2.8 grains of barium bicarbonate per U. S. gallon. The Emperor spring has 0.14 grain of barium bicarbonate per U. S. gallon, the smallest amount of those tested. Hathorn No. 2 carries the largest amount of radium in solution of those examined, but the Emperor does not carry the smallest amount. No connection could be traced between the activities and the quantities of the other salts in solution.

Since these analyses were made, the hydrostatic level of the waters at Saratoga Springs has distinctly changed, owing to the cessation of the extensive pumping for commercial purposes which formerly took place. Accordingly, the flow of many of the wells has increased. Whether this has also affected the radioactivity of the water cannot be predicted with certainty.

BUREAU OF MINES, WASHINGTON

#### THE EFFECT OF FERRIC SALTS AND NITRITES ON THE ORTHO-TOLIDINE AND STARCH-IODIDE TESTS FOR FREE CHLORINE

By J. W. ELLMS AND S. J. HAUSER

Received May 29, 1914

The authors in a previous paper<sup>1</sup> have suggested the use of a hydrochloric acid solution of ortho-tolidine in testing for very small quantities of free chlorine or hypochlorites in water, in place of an acetic acid solution, which was first advocated by Earl B. Phelps. The latter proposed the employment of ortho-tolidine as a qualitative test for free chlorine. The authors in the above-mentioned paper have modified the test as indicated and have further developed a colorimetric method for determining the quantity of chlorine present in a water which had been treated with chlorine or with hypochlorites.

The effect produced by the presence of nitrites or iron in a water when using this method has been brought to our attention, and has caused us to make a few experiments, the results of which are tabulated below.

<sup>1</sup> THIS JOURNAL, 5, 915 and 1030.

<sup>1</sup> Jour. Phys. Chem., 9 (1905), 320.

<sup>2</sup> Proc. Roy. Soc., (A) 77 (1906), 472.

For comparative purposes we have made tests with the starch-iodide method also, and thus show to what extent ferric salts and nitrites may interfere with the accuracy of both methods of determination. As it had been suggested that a sulfuric acid solution of ortho-tolidine was less affected by iron salts than one of hydrochloric acid, comparative tests of the two acid solutions have also been made. Comparative tests have been made as well upon the delicacy of the tests for chlorine, when using a sulfuric acid solution of ortho-tolidine in place of a hydrochloric acid solution.

TABLE I—EFFECT OF IRON AS FERRIC CHLORIDE AND FERRIC SULFATE, AND OF NITRITES ON ORTHO-TOLIDINE IN BOTH HYDROCHLORIC ACID AND SULFURIC ACID SOLUTIONS, ALSO THEIR EFFECT ON THE STARCH-IODIDE TEST

EFFECT OF IRON AS $\text{FeCl}_3$				EFFECT OF IRON AS $\text{Fe}_2(\text{SO}_4)_3$				EFFECT OF NITRITES			
Ortho-tolidine in				Ortho-tolidine in				Ortho-tolidine in			
P. p. m. Fe	HCl sol.	$\text{H}_2\text{SO}_4$ sol.	Starch-iodide test.	P. p. m. Fe	HCl sol.	$\text{H}_2\text{SO}_4$ sol.	Starch-iodide test.	P. p. m. N	HCl sol.	$\text{H}_2\text{SO}_4$ sol.	Starch-iodide test.
0.05	None	None	None	0.1	None	None	None	0.01	None	None	Blue
0.07	None	None	None	0.3	None	None	None	0.03	None	None	Deep blue
0.09	None	None	None	0.5	None	None	Trace	0.05	None	None	Very deep blue
0.10	None	None	Trace	0.7	None	None	Pale blue	0.07	Trace	None	Very deep blue
0.20	None	None	Blue	1.0	Trace	None	Deep blue	0.09	0.01	None	Very deep blue
0.50	Faint trace	None	Deep blue	2.0	0.03	0.01	Very deep blue	0.10	0.02	None	Very deep blue
0.70	Trace	Trace	Very deep blue	3.0	0.04	0.01	Very deep blue	0.30	0.03	Trace	Very deep blue
1.00	0.01	0.01	Very deep blue	5.0	0.09	0.02	Very deep blue	0.50	0.05	0.01	Very deep blue
2.00	0.02	0.02	Very deep blue	7.0	Above 0.09	0.03	Very deep blue				

TABLE II—RELATIVE DELICACY OF A SULFURIC ACID SOLUTION OF ORTHO-TOLIDINE AS COMPARED WITH A HYDROCHLORIC ACID SOLUTION

Hydrochloric acid sol. of ortho-tolidine	Sulfuric acid sol. of ortho-tolidine
Cl in p. p. m. added and indicated	Cl in p. p. m. indicated
0.01	None
0.02	Trace
0.03	0.02
0.04	0.03
0.05	0.04
0.06	0.05
0.07	0.06
0.09	0.08

N. B.—Quantitative results expressed in terms of permanent chlorine standards, as described in a previous paper for ortho-tolidine.

These results indicate, so far as the ortho-tolidine reagent is concerned, that the presence of ferric iron or of nitrites in quantities that are not infrequently found in water and sewage, might, if their presence was not suspected, give the impression that chlorine or hypochlorites were present in the water. Interferences of this kind are common enough in practically every method of chemical analysis, but incorrect deductions may be easily guarded against by careful qualitative tests. The presence of iron is easily ascertained, but as the table shows, the quantity which must be present to produce a color is approximately 1.0 part per million, or an amount not usually found in surface waters, but which might be present in ground waters. High nitrites in surface waters, unless badly polluted, are not likely to be found, although sewage and especially sewage effluents may contain them in amounts that would interfere with the accuracy of the method. It will be noted that the starch-iodide method is as much, if not more, affected by the presence of nitrites and ferric salts than is the ortho-tolidine method.

It apparently is true from these tests that a sulfuric acid solution of ortho-tolidine is not as much affected by ferric salts and by nitrites as is the hydrochloric acid solution. However, a sulfuric acid solution of ortho-tolidine is not as easily prepared as one of hydrochloric acid, and from the comparisons made in Table II, does not seem to be able to indicate quite as small amounts of chlorine as does the hydrochloric acid solution. It hardly seems worth while

to substitute the former for the latter because it is less affected by ferric salts and nitrites.

In the authors' previous paper it was quite clearly stated that it was believed that the oxidation of the ortho-tolidine was the cause for the color changes observed. If this is true all oxidizing agents will probably produce, under proper conditions, color changes in solutions of ortho-tolidine. In proof of this the authors have made further experiments with a number of oxidizing agents and have found this to be the case without exception, if the proper concen-

trations of the oxidizing compound and of acid were employed. The late Dr. L. P. Kinnicutt<sup>1</sup> in quite a thorough investigation of the effect of oxidizing agents on ortho-tolidine showed that ozone, nascent oxygen, sodium nitrite, ammonium persulfate, ferric chloride, ferric alum, potassium permanganate, potassium bichromate, sodium peroxide and lead peroxide gave color reactions with ortho-tolidine.

The authors in their previous paper noted the color reactions produced by bromine, iodine and nitric acid as well as by potassium bichromate and potassium permanganate, which latter were mentioned by Kinnicutt. In recent experiments the authors have found that hydrogen peroxide, with which Kinnicutt was unable to produce a color reaction with ortho-tolidine, will also act similarly to all the other oxidizing compounds, if the concentration of the acid in the solution is great enough.

The probability of the presence of any of the oxidizing agents mentioned, excepting ferric salts and nitrites in natural waters, or even in sewage is rather remote. With proper precautions the ortho-tolidine method is applicable to the usual conditions under which chlorine and hypochlorites are tested for in water.

CINCINNATI FILTRATION PLANT  
CINCINNATI, OHIO

### A NEW METHOD FOR THE DETERMINATION OF HYDROCYANIC ACID AND THE ALKALI CYANIDES

By G. E. F. LUNDELL AND J. A. BRIDGMAN

Received April 2, 1914

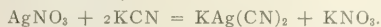
One gravimetric and five different volumetric methods have already been proposed for the above named determination. The authors' excuse for bringing out still another method is that the proposed method is superior to the older methods in several important respects. For the sake of comparison, the following

<sup>1</sup> Data published as part of testimony taken in suit of Jersey City vs. East Jersey Water Co.

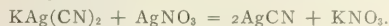
very brief reviews of the existing methods are given:

In the gravimetric method the cyanide is precipitated in a weak nitric acid solution as silver cyanide which is either dried at 100° C. and weighed as such, or ignited and weighed as silver. This method is open to at least three objections: (1) It requires too much time. (2) The results obtained are invariably too high since chlorides and sulfocyanates, which are commonly present in commercial cyanides, are also precipitated by silver nitrate in a weak nitric acid solution. (3) When a large number of determinations are made, the method is too expensive.

LIEBIG'S METHOD<sup>1</sup> depends on the fact that soluble potassium silver cyanide is first formed when an aqueous solution of a cyanide is treated with a silver nitrate solution,

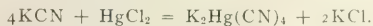


When silver nitrate in excess of that required for the above reaction has been added, the potassium silver cyanide is decomposed with the separation of insoluble silver cyanide which renders the solution turbid.

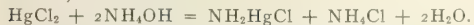


Therefore standard silver nitrate solution is added to the prepared cyanide solution until a permanent opalescence is obtained. The objections to this method are at least three in number: (1) The results obtained are usually too high since alkali carbonates, sulfocyanates and ferrocyanides delay the end point. (2) The titration requires a perfectly clear solution. (3) When a large number of determinations are made the method is costly, each titration requiring 50 cc. 0.1 *N* AgNO<sub>3</sub> solution costing about 2 cents.

HANNAY'S METHOD<sup>2</sup>—An ammoniacal solution of a cyanide when treated with mercuric chloride will give no precipitate until the completion of the reaction expressed by the equation



When the potassium cyanide has been used up in accordance with the above reaction, further addition of mercuric chloride causes a precipitation of mercurammonium chloride which imparts an opalescence to the solution,



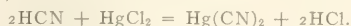
Hence a standard mercuric chloride solution is added to the prepared cyanide solution until a permanent opalescence is produced. This method gives good results in most cases. Some objections are: (1) The difficulty experienced in correctly standardizing the mercuric chloride solution. (2) The titration requires a perfectly clear solution. (3) Ferrocyanides delay the end point, thereby causing high values on samples containing this impurity.

FORDOS AND GELIS' METHOD<sup>3</sup> is based on the behavior of iodine towards potassium cyanide,



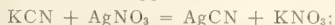
A standard iodine solution is added to the prepared cyanide solution until a permanent yellowish tinge is obtained. The results obtained by this method are not accurate and the interferences are numerous.

ANDREW'S METHOD<sup>4</sup>—The diluted solution of hydrocyanic acid or a simple cyanide is made just alkaline to paranitrophenol. At this point all of the original hydrocyanic acid or cyanide is present as hydrocyanic acid since this acid is without effect on the indicator. The solution is then treated with an excess of mercuric chloride,



Upon the completion of the reaction, the liberated hydrochloric acid is titrated with 0.1 *N* sodium hydroxide. This method works well with pure cyanides but is not accurate when used on commercial material. Then too the method takes too much time.

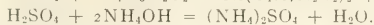
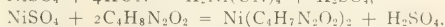
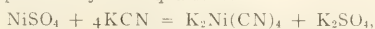
VIELHABER'S METHOD<sup>5</sup>—In this method, the cyanide solution is made alkaline by the addition of magnesium hydroxide suspended in water. After the addition of a few drops of chromate indicator, the solution is titrated with 0.1 *N* silver nitrate until a permanent red color appears,



This method is not accurate. Besides the inherent error of the method, high results are obtained whenever chlorides, sulfocyanates or ferrocyanates are present.

#### THE NEW METHOD

Briefly stated, the new method consists in titrating an ammoniacal cyanide solution containing a small quantity of dimethyl glyoxime, with a standard nickel ammonium sulfate solution until a permanent red precipitate is produced. The reactions involved are expressed by the equations:



No permanent red precipitate of nickel dimethyl glyoxime is formed until all of the cyanide has been used up in the reaction expressed by the first equation. The ammoniacal cyanide solution is used since free sulfuric acid hinders the precipitation of nickel dimethyl glyoxime.

#### SOLUTIONS REQUIRED

1—STANDARD NICKEL SOLUTION, prepared by dissolving 15.3 grams of nickel ammonium sulfate in water containing 2 cc. of concentrated sulfuric acid, diluting to one liter and standardizing as directed below.

2—DIMETHYL GLYOXIME SOLUTION, prepared by dissolving 8.9 grams of dimethyl glyoxime in one liter of 95 per cent alcohol.

#### STANDARDIZATION OF NICKEL SOLUTION

Unless the percentage purity of the nickel ammonium sulfate is known, the prepared nickel solution must be standardized as follows: 25 cc. portions are diluted with distilled water to 200 cc., treated with 0.2 gram tartaric acid and heated to boiling. Glyoxime solution sufficient to precipitate all of the nickel is then added. If the glyoxime solution has been made

<sup>1</sup> *Ann.*, **77** (1851), 102.

<sup>2</sup> *J. Chem. Soc.*, **33** (1878), 245.

<sup>3</sup> *J. prakt. Chem.*, **59** (1899), 255.

<sup>4</sup> *Chem. News*, **88** (1903), 239.

<sup>5</sup> *Arch. Pharm.*, [3] **13**, 408.



up according to the formula above, 30 cc. should be sufficient. After the addition of the glyoxime, the solution is made slightly alkaline with ammonia, boiled for two minutes and then set aside to digest for one-half hour. The precipitate is caught on a tared Gooch crucible, washed with 200 cc. of hot water, dried for 45 minutes at 120° C. and weighed. The weighed precipitate contains 20.31 per cent nickel. From the equations given above the hydrocyanic acid or the potassium cyanide titre of the solution can readily be calculated. If a chemically pure potassium cyanide is at hand, the above titres can be determined directly by titrating weighed portions as directed in the "Method of Analysis" given below.

#### METHOD OF ANALYSIS FOR ALKALI CYANIDES

Five grams of the sample are dissolved in water and diluted to exactly 500 cc. Pipetted 50 cc. portions of this solution are diluted with an equal volume of water, treated with 1 cc. of ammonium hydroxide and 0.5 cc. of the dimethyl glyoxime solution and then titrated with the standard nickel solution until a permanent red precipitate is produced. The color play toward the end of the reaction resembles the methyl orange end point observed in titrating an alkaline solution with an acid solution. The nickel ammonium sulfate solution may be added rapidly at first, provided the cyanide solution is vigorously stirred; toward the end point the addition should be slower and the stirring more rapid. If more than 0.5 cc. of glyoxime is used, the end point shows a tendency to appear too soon unless the addition of the standard solution is slow and the agitation of the solution very brisk. The cyanide dilution may be varied without serious effect; however, the method works better when the volume is approximately 100 cc. A large excess of ammonium hydroxide delays the end point; 1 to 5 cc. in the volume specified does no harm. A titration requiring 50 cc. of the standard solution costs one-fifth of a cent.

In titrating solutions which contain hydrocyanic acid, a measured volume of solution is made alkaline with ammonium hydroxide and then treated as above.

Table I shows the values obtained on different cyanide samples by the new method and by two of the older methods.

TABLE I—ANALYSES BY DIFFERENT METHODS—PERCENTAGES HCN

Sample	Gravimetric method(a)	New method	Liebig's method
1 KCN.....	39.35	39.16	39.55
2 KCN.....	39.25	39.00	39.57
3 KCN.....	40.75	40.71	40.79
4 NaCN.....	33.58	33.55	33.70
5 HCN solution.....	0.59	0.595	0.60
6 Cherry laurel water.....	0.050	0.050	0.051
7 Oil of bitter almond water.....	0.076	0.076	0.077

(a) Corrected for chlorides.

The results obtained by all three methods check closely on Samples 3, 4, 5, 6 and 7. The values on Samples 1 and 2 are not in such good agreement but it is seen that the new method checks up the corrected gravimetric method better than does Liebig's method. Qualitative tests showed small amounts of sulfocyanates and ferrocyanides, both of which would cause high results in the gravimetric method and Liebig's method.

Table II demonstrates the accuracy of the new method in the presence of possible impurities in commercial cyanide samples:

TABLE II—TITRATIONS OF MIXTURES

50 cc. of 1 per cent KCN solution used in each titration			
Reagent added	Ce. nickel ammonium sulfate percentage required	Reagent added	Ce. nickel ammonium sulfate percentage required
None.....	49.45	0.00	49.47
1 g. KCN.....	49.45	0.00	49.39
1 g. KCN.....	49.46	+0.02	49.42
1 g. K <sub>2</sub> CO <sub>3</sub> .....	49.41	-0.08	49.5
10 g. K <sub>2</sub> CO <sub>3</sub> .....	49.55	+0.20	50.02
20 g. K <sub>2</sub> CO <sub>3</sub> .....	49.62	+0.34	50.02
1 g. K <sub>2</sub> SO <sub>4</sub> .....	49.43	-0.04	49.48
1 g. NH <sub>4</sub> Cl.....	49.42	-0.06	50.75
1 g. NaCl.....			+0.04
1 g. NH <sub>4</sub> NO <sub>3</sub> .....			-0.12
1 g. NaHCO <sub>3</sub> .....			-0.06
0.1 g. KOH.....			0.00
1 g. KOH.....			+1.15
0.3 g. CaCN <sub>2</sub> .....			+0.02
0.1 g. K <sub>4</sub> Fe(CN) <sub>6</sub> .....			+0.06

This table demonstrates the remarkable freedom of the method from interfering substances. KOH and K<sub>4</sub>Fe(CN)<sub>6</sub> interfere when present in large amounts; the small quantities usually present in commercial cyanides have practically no effect at all.

Table III shows the accuracy of the method in the presence of the double cyanides commonly used in electroplating.

TABLE III—TITRATIONS IN PRESENCE OF DOUBLE CYANIDES

Double cyanide present	G. KCN added	G. KCN found	Percentage error
KAg(CN) <sub>2</sub> .....	0.1208	0.1205	-0.25
KCu(CN) <sub>2</sub> .....	0.1915	0.1906	-0.47
K <sub>2</sub> Zn(CN) <sub>4</sub> .....	0.3520	0.4612	+31.02

It is seen that the method gives only the "free" cyanide in silver and copper cyanide solutions. Experiments show that more than the free cyanide is obtained in zinc cyanide solutions, the end point occurring when the Zn : KCN ratio is approximately 1 : 0.6. In copper and silver cyanide solutions Liebig's method works the same as the new method. In zinc cyanide solutions Liebig's method gives the total cyanide, that is, the free cyanide plus the cyanogen in the zinc double cyanide. Hannay's method gives the total cyanide in all three cases. This is a disadvantage because only the free cyanide is ordinarily desired.

#### SUMMARY

The new method for the determination of hydrocyanic acid and the alkali cyanides consists in making the cyanide solution ammoniacal, then adding a small amount of methyl glyoxime solution and finally titrating this prepared solution with a standard nickel ammonium sulfate solution until a permanent red precipitate is produced. The preceding pages show that the new method is accurate, free from ordinary interferences, usable in cloudy solutions, rapid, cheap and of value in titrations of double cyanides.

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#### A METHOD FOR THE RAPID QUANTITATIVE ANALYSIS OF BRONZE AND BRASS<sup>1</sup> (Pb, Cu, Sn, Sb, Fe and Zn)

By RICHARD EDWIN LEE, JOHN P. TRICKEY AND WALTER H. FEGELY

#### INTRODUCTION

The method of analysis reported in this paper is the outgrowth of an investigation that was undertaken as the result of a request made to one of us sometime

<sup>1</sup> Presented at the 49th meeting of the American Chemical Society, Cincinnati, April 6-10, 1914.

ago to take charge of some "control" work for a large company manufacturing bronze metal in various forms. Most of the metal is sold on specification. The alloy supplied by this firm varies in composition as follows: Cu, 65 to 69 per cent; Pb, 25 to 30 per cent; Sn, 5 to 6 per cent; Fe, 0.1 to 0.3 per cent; Zn, 1.5 to 3 per cent. The requirements were that the analysis be accurate to 0.2 per cent and that the time consumed in making the complete analysis should not exceed one hour, preferably 45 minutes.

On receipt of this request the authors began immediately to make a careful survey of the literature relating to the analysis of bronze and brass in the hope that it would be possible to find a method adapted to their needs. Over two months were devoted to testing the various proposed methods with 'known mixtures' of the metals comprising the alloy. The authors hesitate to say whether the fault lay with themselves or was inherent in the methods, but most discouraging results were obtained although each method was tested repeatedly with the exercise of much care. We were finally confronted with the following perplexing situation; on the one hand, such methods as were found to give the required accuracy were too long and tedious; on the other hand, the few methods proposed for rapid analyses failed in our hands to give not only the desired accuracy, but the accuracy claimed for the methods by their respective authors.

This experimental survey, however, was not without value, as it rendered possible not only the detection of inaccuracies in many of the recommended procedures, but the selection of the best processes involved in such of the proposed methods as most closely approximated our wants. Furthermore, it facilitated the formulation of conditions best adapted to securing the desired end.

Early in the investigation it became obvious that it would contribute greatly to the rapidity of the determinations if a method could be formulated which would provide for the using of a separate portion of the alloy for each determination. The more accurate of the proposed methods are as a rule, open to the serious objection that one portion of the alloy is used for several determinations. Such procedure, however, is time-consuming. In the method of analysis proposed in this paper all the metals are determined in separate portions of the alloy with the exception of zinc which is determined in the filtrate from the iron if the latter is present. When the iron is absent from the sample the zinc is determined in a separate portion in about thirty minutes.

The authors make no particular claim to originality for the scheme of analysis submitted herewith as most of the methods are based upon reactions familiar to all chemists. Furthermore, some of them have been employed by Low, Demorest, P. H. Walker and Whitman and other well known contributors to industrial analysis as a basis of standard methods for *single* determinations. However, the modifications of the selected procedures and their application to the complete analysis of bronzes of the stated composition, the study of the sources of error and the conditions most favorable for procuring the desired results by means of the

adopted procedures together with the formulation of such new processes as were necessary to articulate the different procedures, are some of the problems which have been attacked.

The accuracy of the methods is shown by the experimental results recorded in Part II, Test Experiments. As a further confirmation of the dependability of the method it may be noted that the procedure described herein has been used with equally good results not only by the students in this laboratory but also by the chemists in one large testing laboratory<sup>1</sup> for a period of nearly three months.

#### PART I.—METHOD OF ANALYSIS

##### DETERMINATION OF LEAD

**PROCEDURE**—To 0.5 gram of the alloy in a 300 cc. Erlenmeyer flask, add 12 cc. of water containing 4 grams of tartaric acid, and then 4 cc. of conc.  $\text{HNO}_3$ . Place on a hot plate to dissolve the alloy quickly. (The solution should be perfectly clear; if not, reject it and repeat the procedure.) Remove the solution from the hot plate, allow to cool for 1 to 2 minutes, add 10 cc. conc.  $\text{H}_2\text{SO}_4$ , and then heat on hot plate until all nitrous fumes are expelled. (Caution: Care must be exercised not to carry the procedure beyond this stage or the tartaric acid will be decomposed.) Dilute with 100 cc. of cold water, add 75 cc. of ethyl alcohol, shake, allow to stand for 2 or 3 minutes, filter through a weighed gooch crucible, wash with water to which a little  $\text{H}_2\text{SO}_4$  has been added, until the precipitate is white and then wash out acid with alcohol. Reject the filtrate. Dry the precipitate in crucible on hot plate, and then heat to dull redness with the Bunsen burner for a few minutes. Cool and weigh as  $\text{PbSO}_4$ .

$$\text{Wt. PbSO}_4 \times 0.683 = \text{wt. Pb}$$

**NOTES**—1—In order to prevent occlusion and adsorption of the Cu salts by the lead sulfate precipitate, it was found necessary to make the solution from which the lead precipitate is separated by filtration, relatively large. The solution of the lead sulfate is prevented by the addition of alcohol.

2—In case the alloy contains a small percentage of lead, it is advisable, of course, to use a relatively large amount of the sample. If this is done, the quantities of the reagents employed, including water and alcohol, should be increased proportionately. The reasons for this procedure are obvious. In the first place, unless the volume of the solution is made larger the concentration of the Cu and other metals present becomes very large owing to the use of larger amounts of sample. This will increase the error due to occlusion and adsorption as mentioned in Note 1. In the second place, in order to preserve the proper concentration of sulfate ions for the complete precipitation of Pb in this larger volume of solution it is necessary to use larger amounts of the reagent, sulfuric acid.

##### DETERMINATION OF COPPER

**PROCEDURE**—Place 0.5 gram of the alloy in a 400 cc. beaker, add 5 to 10 cc. of dilute  $\text{HNO}_3$  (1-1), cover beaker with a watch glass until violent action ceases, then remove watch glass and evaporate on hot plate to syrupy consistency. Dilute to about 200 cc. and add KOH solution until a small precipitate of copper hydroxide persists after thorough stirring. Now add acetic acid until the copper precipitate is completely

<sup>1</sup> The Meadville Testing Laboratory, Meadville.

dissolved, then add a small excess of the acid. Cool the mixture to tap-water temperature, then add 40 cc. of the KI solution (100 grams to 1 l.) and 5 cc. of starch solution, and titrate immediately with standard  $\text{Na}_2\text{S}_2\text{O}_3$  solution until the blue color disappears.

NOTES—1 It has been pointed out by Walker and Whitman<sup>1</sup> that the results obtained by following Low's iodide method<sup>2</sup> are uniformly a little low. They add "this error is not due to the method which gives exceedingly accurate results, but to the fact that nearly 6 per cent of the copper is not precipitated as cuprous oxide. This loss is uniform for if we add 6 per cent of the copper determined, the result will be the per cent of the copper in the alloys." This is undoubtedly true. Their further statements, however, that when an alloy containing 5 per cent of copper is decomposed by nitric acid, evaporated to dryness, taken up with nitric acid and filtered, the error in determining the copper in the filtrate will frequently be 0.5 to 0.7 per cent, cannot be confirmed by our experience. By following the proposed method of standardization and analysis, which is essentially Low's method we have been able to check within 0.1 per cent repeatedly.

2—Provision has not been made in the method as formulated for the separation of copper from any other metals, yet care must be exercised to exclude from the solution prepared for titration any substances which will either liberate or absorb iodine. Therefore, free Cl, free Br, nitrous oxides, ferric ions, and As and Sb in the 'ous' condition must be absent.

Ferric ions may be removed by adding ammonium fluoride, which interacts with the former to produce ferric fluoride. This latter substance which is only slightly ionized has little or no oxidizing power and, therefore, cannot liberate iodine under the existing conditions.

The trivalent arsenic and antimony, if present, must be oxidized to the pentavalent condition by the addition of bromine. Excess of bromine must be removed by boiling the solution before titrating.

No other elements interfere with the procedure.

3—Pb, Bi, and Cd, if present, interact with the KI and form the corresponding yellow insoluble iodides. This causes no trouble, however, in fact many chemists regard the presence of one or more of these metals as a distinct advantage as the presence of the yellow precipitate assists the operator in securing uniform end points. In this laboratory it is customary to add a few cc. of a solution of lead acetate to the solution to be titrated if it is known that Pb is not present.

4—In order that the liberated iodine may be held in solution it is necessary to use rather large excess of KI. This procedure increases the speed of the reaction.

5—The presence of an excess of inorganic acid interferes with the procedure. It should be remembered, however, that unless the solution contains a sufficient excess of acetic acid the end point will not be sharp.

6—The solution should always be cooled to tap water temperature just before the KI solution is added.

7—It should be remembered that the Sn present will make an insoluble residue in the solution prepared for titration.

#### DETERMINATION OF TIN (AND Sb)

PROCEDURE—Weigh 0.5 g. of the alloy into a 400 cc. beaker, add 5 to 10 cc. of dil.  $\text{HNO}_3$  (1-1), cover with a watch glass until violent action ceases, then remove cover and evaporate to a paste on hot plate. Add 15 cc. of dil.  $\text{HNO}_3$ , boil for several minutes and dilute to about 200 cc. Boil for a few minutes, filter through a weighed Gooch crucible, wash with hot nitric acid

wash, and then with hot water. Pour the filtrate into a 500 cc. beaker and reserve for check determination of copper. Dry the crucible and contents on hot plate and then ignite at red heat for ten minutes. The ignited residue consists of  $\text{SnO}_2$  and any Sb (as  $\text{Sb}_2\text{O}_3$ ) which may have been present in the alloy.

Wt.  $\text{SnO}_2$  (and  $\text{Sb}_2\text{O}_3$ )  $\times 0.788 = \text{wt. Sn (and Sb)}$

NOTES—1—The results obtained by this method are usually a little high, owing to the fact that the precipitate frequently contains traces of the oxides of Cu, Sb, and Pb. However, the digestion of the dried residue in dilute nitric acid and the final separation of the precipitate from a large volume of solution, tend to reduce errors from this source. The precipitate will also contain any phosphorus that is present in the sample.

2—Much time and energy were consumed in an effort to obtain a volumetric method for determining tin in a separate portion of the alloy. One of the most attractive volumetric methods for making this determination is Walker and Whitman's modification<sup>1</sup> of Low's iodimetric method. Our efforts, however, to adapt it to our scheme of analysis were without success. The chief obstacle to its application to the rapid analysis of bronze is the presence of relatively large percentage of Cu in the alloy. The method, however, was found to give excellent results when used in making analyses of Babbitt metal if the percentage of Cu in the alloy was small; but if the percentage of Cu was large the results came high, owing to the fact that during the reduction of the Sn the Cu was reduced to cuprous chloride which takes up a portion of the iodine when the solution is finally titrated. Our results in regard to the errors introduced by the titration of Sn in the presence of Cu agree with those obtained by Ibbotson and Aitchison.<sup>2</sup>

#### (CHECK DETERMINATION OF COPPER)

PROCEDURE—Cool the filtrate from the Sn determination, add KOH solution until a small precipitate of copper hydroxide persists after thorough stirring. Add acetic acid until the copper precipitate is completely dissolved, then add a small excess of the acid. Follow directions as given under Determination of Copper.

#### DETERMINATION OF ANTIMONY

PROCEDURE—Weigh out 0.5 gram of the fine drillings of the alloy into a 300 cc. Kjeldahl flask, add 25 cc. of conc. sulfuric acid and heat over the bare flame of a Bunsen burner. Keep the acid at its boiling point until the solution is clear or the residue is white. Cool, add 100 cc. of water, boil for several minutes and transfer the contents of the flask to a 400 cc. beaker. Dilute to 200 cc., heat to  $70^\circ\text{C}$ . ( $158^\circ\text{F}$ .) and titrate with a standard  $\text{KMnO}_4$  solution. The permanganate solution should be added rapidly until the permanganate color persists, then add several cc. in excess. Stir the solution vigorously, and then titrate with a standard solution of ferrous ammonium sulfate until the pink color just disappears.

NOTES—1—Although antimony is not found in the majority of bronzes and brasses it frequently occurs alloyed with variable percentages of lead, tin, copper and iron. Therefore, in order to make the present scheme of analysis as wide as possible in its application and thereby increase its usefulness, it was deemed advisable to incorporate a method for the rapid determination of Sb.

2—The method is at once recognized as a modification of

<sup>1</sup> THIS JOURNAL, 1 (1909), 519

<sup>2</sup> Jour. Am. Chem. Soc., 24 (1902), 1082.

<sup>1</sup> THIS JOURNAL, 1 (1909), 519.

<sup>2</sup> Chem. News, 107 (1913), 109, also C. A., 7 (1913), 2025, 8 (1914), 476.



Low's well known method.<sup>1</sup> The chief difficulty we experienced in fitting it to our scheme of analysis was the matter of securing Sb in a suitable condition in sulfuric acid solution. Alloys containing a high percentage of copper resist solution by the usual procedure. Nitric acid is eliminated as a solvent because of its oxidizing action; and HCl and KClO<sub>3</sub> are ineffective unless the treatment is greatly prolonged. Finally, the not-entirely satisfactory method of decomposing the alloy in conc. sulfuric acid in a Kjeldahl flask exposed to the bare flame of a Bunsen burner was adopted. Complete decomposition is usually effected in ten to twenty minutes, after which the determination may be readily finished in 10 minutes.

After one or two trials, it will probably be found that the blue color imparted to the solution by the presence of the copper does not hinder the determination of the exact end point when the permanganate is added.

3—Demorest has pointed out in an excellent paper<sup>2</sup> that it is necessary to employ a large excess of potassium permanganate to complete the oxidation of the Sb. It is not best to have HCl present when the antimony is titrated as the end point is made very transient by its presence.

#### DETERMINATION OF IRON AND ZINC

PROCEDURE—To 0.5 gram of the alloy in a 400 cc. beaker add sufficient dilute HNO<sub>3</sub> (1-1) to dissolve the sample. Heat on hot plate until the alloy is thoroughly decomposed, then evaporate the solution just to dryness. Add 10 cc. of conc. HCl and 100 cc. of water, heat to about 70° C. and pass H<sub>2</sub>S through the mixture until all the Pb, Cu, Sn, and Sb (Cd, etc.) are precipitated. Filter, using a Buchner funnel with an asbestos mat, wash the precipitate with water. The filtrate which contains the iron and zinc should be transferred to a 500 cc. beaker.

NOTE—A drop of this filtrate should be transferred to a spot plate and tested with a drop of potassium ferrocyanide for the presence of Cu and Fe which are interfering substances and if present in weighable quantities they should be removed. If Cu is present which will be indicated by the presence of red coloration, treat the filtrate again with hydrogen sulfide and filter; if Fe is present which will be indicated by the appearance of a blue coloration, proceed as directed under (2), Iron and Zinc.

1—ZINC, IF FE IS ABSENT—Dilute the filtrate to 200 cc., heat to 70° C. and titrate with standard potassium ferrocyanide, using ferric chloride or uranyl nitrate as an indicator. The titration should be performed slowly and with constant stirring in order to obtain the most satisfactory results. Continue to add the ferrocyanide until a drop of the solution in the beaker shows a bluish green tinge (brown tinge when uranyl nitrate is used as an indicator) when tested on a white porcelain plate with a drop of ferric chloride after standing a few seconds. The quantity of the standard solution which is required to produce a good end point in the blank determination made at the time of standardizing the solution, must be subtracted from the amount of standard used in making the determination.

NOTE—1—Correction for Blank. As the indicators are not very sensitive under the imposed conditions it is necessary to determine the excess of standard solution required to effect the color change of the indicator used. A 'blank' must be run, therefore, using the same quantities of reagents under corresponding conditions of volume, temperature and acidity.

<sup>1</sup> THIS JOURNAL, 6 (1913), 842.

<sup>2</sup> Ibid., 6 (1913), 842.

2—If the solution turns blue during the titration, it is an indication of the presence of small quantities of iron.

2—IRON AND ZINC—Add 2 cc. of concentrated HNO<sub>3</sub> to the filtrate to oxidize the Fe, heat to boiling, add 25 cc. of 5N NH<sub>4</sub>Cl and then NH<sub>4</sub>OH until the odor of the reagent barely persists after boiling the mixture for one minute. Filter off the Fe(OH)<sub>3</sub> and ignite. Weigh as Fe<sub>2</sub>O<sub>3</sub>.

NOTES—1—Zinc is completely precipitated from HCl solutions by potassium ferrocyanide as white zinc ferrocyanide. Such metals as Pb, Cu, Sn, Fe and Mn are also precipitated by this reagent, and therefore must be removed before the Zn is titrated.

2—The acid solution must not contain free Cl, free Br or the oxides of chlorine as these substances decompose ferrocyanide.

3—Care must be taken to conduct the standardization as well as all determinations under corresponding conditions with particular reference to volume, temperature, acidity, amount of ammonium salts and the rate of titration. Furthermore, it is imperative that the titration be conducted slowly and with constant stirring of the solution. If this precaution is not observed the end point will be reached apparently before all the zinc is precipitated.

#### PART II—TEST EXPERIMENTS

In order to make a final test of the accuracy and general applicability of the procedures recommended in this paper, five series of experiments—each series consisting of six separate determinations were made. In making this test, the results of which are reported herewith, a standard bronze alloy was used unless there is a note to the contrary. Equally good results were obtained when known mixtures were employed.

##### SERIES I—LEAD

Number of experiment	Wt. of sample Grams	Wt. of Pb present Gram	Wt. of Pb found Gram	Error percentage composition
(1).....	1.0055	0.0467	0.0469	00.02%
(2).....	1.0005	0.0464	0.0465	00.01%
(3).....	0.9995	0.0463	0.0464	00.01%
(1).....	0.2013	0.1562	0.1559	00.10%
(2).....	0.2114	0.1639	0.1642	00.15%
(3).....	0.2266	0.1757	0.1754	00.15%

A standard Babbitt metal was employed in making the last three determinations reported in the foregoing series.

##### SERIES II—COPPER

Number of experiment	Wt. of sample Gram	Wt. of Cu present Gram	Wt. of Cu found Gram	Error percentage composition
(1).....	0.5018	0.3042	0.3047	00.10%
(2).....	0.5133	0.3112	0.3116	00.08%
(3).....	0.5212	0.3160	0.3160	00.10%
(4).....	0.4956	0.3009	0.3001	00.18%
(5).....	0.5120	0.3104	0.3107	00.06%
(6).....	0.5094	0.3088	0.3084	00.08%

##### SERIES III—TIN

Number of experiment	Wt. of sample Grams	Wt. of Sn present Gram	Wt. of Sn found Gram	Error percentage composition
(1).....	1.0000	0.0238	0.0242	00.04%
(2).....	1.0000	0.0238	0.0251	00.13%
(3).....	1.0000	0.0238	0.0252	00.14%
(1).....	0.5000	0.0119	0.0120	00.02%
(2).....	0.5000	0.0119	0.0123	00.08%
(3).....	0.5000	0.0119	0.0122	00.06%

##### SERIES IV—ANTIMONY

A standard Babbitt metal, containing 77.53 per cent of Pb, 0.58 per cent of Cu, 10.03 per cent of Sn, and 11.65 per cent of Sb, was employed in making the tests, the results of which are recorded in the following series. In the first two determinations the Pb was removed as PbSO<sub>4</sub> before titrating with KMnO<sub>4</sub>; in the following four determinations the titration was conducted in the presence of the PbSO<sub>4</sub>; and in the

last two determinations the titration was made in the presence of both Pb and Cu salts.

Number of experiment	Wt. of sample Gram	Wt. of Sb present Gram	Wt. of Sb found Gram	Error percentage composition
(1).....	0.3000	0.0350	0.0349	00.03%
(2).....	0.3000	0.0350	0.0349	00.03%
(1).....	0.3000	0.0350	0.0349	00.03%
(2).....	0.3000	0.0350	0.0359	00.03%
(3).....	0.3027	0.0353	0.0354	00.03%
(4).....	0.3027	0.0353	0.0356	00.09%
(1).....	0.0327	0.0353	0.0354	00.03%
(2).....	0.0327	0.0353	0.0354	00.03%

The above results indicate that the presence of the Pb and Cu salts do not interfere with the titration of Sb with  $\text{KMnO}_4$ .

#### SERIES V—ZINC

Number of experiment	Wt. of sample Gram	Wt. of Zn present Gram	Wt. of Zn found Gram	Error percentage composition
(1).....	0.4985	0.1497	0.1492	00.10%
(2).....	0.4969	0.1492	0.1497	00.11%
(3).....	0.4975	0.1494	0.1497	00.06%
(4).....	0.4977	0.1494	0.1495	00.02%
(5).....	0.4979	0.1495	0.1496	00.02%
(6).....	0.5004	0.1503	0.1503	00.04%

#### PART III—SUMMARY

I—A survey of a large number of proposed methods for the analysis of bronze and brass has been made. The majority of the methods have been found to be too long and elaborate; or if in the class of rapid methods, too inaccurate to be suitable even for control work.

II—A method has been proposed for the analysis of bronze and brass containing Pb, Cu, Sn, Sb, Fe, and Zn by which the determinations may be made with greater rapidity than any other methods of analysis known to the authors. Working with the usual laboratory facilities it has been found that after the samples have been weighed the determinations of Pb, Sn and Sb in three different alloys can be easily completed in one and one-half to two hours.

III—The determinations made by this method not only agreed among themselves but they were more accurate than those made by the longer methods. The maximum error of any determination in any series was 0.15 per cent. The average error, however, is much less.

IV—The accuracy and general applicability of the proposed method has been shown by the series of test experiments, and further confirmed by the report of one commercial laboratory where the method has been constantly employed for nearly three months.

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#### THE CHEMICAL EVALUATION OF WOOD FOR PULP<sup>1</sup>

By M. L. GRIFFIN

In a previous paper,<sup>2</sup> the author showed the inadequacy of the cord measure as a unit for valuing pulp wood, resulting in great variation in the solid volume, due to various factors. As a better standard he advocated a solid unit, the cubic foot, and illustrated how such a unit could be adapted in practice without inconvenience. A unit of weight as a still more reliable basis was also advocated. There remains the

<sup>1</sup> Presented before the Maine Section of the A. C. S., Auburn, May 1, 1914.

<sup>2</sup> See abstract, *This Journal*, 6, 163.

valuation according to the amount of fiber wood will yield, which is the chief concern of manufacturers of chemical pulps.

To make effective any of these units as a basis for evaluating wood for pulp we must resort to an efficient system of sampling which will be truly representative. Such a system was described in the author's former paper.

The need of such a basis for valuing wood is at once apparent when we stop to think of the great variation in the quality of the same species, depending upon its habit and conditions of growth. Poplars of our northern states differ greatly from those of the middle southern states. The measurement of value by cord or solid contents takes no account of yield in pulp. Other species of similar external characteristics are often mixed in, as Bass wood with poplar, and fir and hemlock with spruce. Such mixtures in late years have been permitted, when the characteristics are near enough to cause no trouble in cooking. Aside from these differences in species, and habit of growth, there is the quality of the wood, as such, which should be taken into account in its bearing on yield of pulp. Wood is subject to disease and decay and all such defective wood will not give the normal product.

With a view to discovering the influence of these various factors upon the yield, a large number of determinations of the cellulose were made by the Cross and Bevan chlorination method.

PROCEDURE—The stick to be tested was quarter sawn, and the sample was obtained by planing thin shavings from the face of the quarter. In this way the sample would include a part of the growth from the center to the bark. We found such thin shavings much more satisfactory than any other form. Three grams of the shavings, previously dried at 100° C., were boiled for about half an hour in 1 per cent sodium hydrate. The mass was then well washed and squeezed and placed under a bell-glass, into which was led a slow stream of chlorine gas. Complete conversion of the lignone usually followed in one hour's exposure to the gas. It was then well washed to remove hydrochloric acid and impurities and placed in a two per cent solution of sodium sulfite containing 0.2 per cent sodium hydrate, and boiled for about five minutes. The fiber was then well washed with hot water and this treatment with sodium sulfite and hydrate repeated if found necessary. The fiber was found almost pure and nearly white.<sup>1</sup> It was then dried, weighed and results calculated.

Table I gives the characteristics of 24 samples of mixed spruce and balsam fir from Montmorency in Canada. The samples were selected to show the various factors influencing the yield in chemical fiber. Eight of these samples were chosen from wood of recognized good quality for comparison. From a review of the table and the samples we observe:

I—That density of annual ring growth is not necessarily proportional to specific gravity (see Nos. 1, 7, 9, 23 and 24) and that specific gravity is not pro-

<sup>1</sup> To remove the last residues of non-cellulosic matter, it may be bleached with hypochlorite or permanganate. If with the latter, it will be necessary to wash with a weak solution of sulfurous gas.

portional to yield of fiber. This latter is also shown by Nos. 2, 8, 21 and 22, where yield is fairly regular and specific gravity is irregular. This would indicate that habit and environment have much to do with the quality of wood.

II—We can establish very well the influence of incipient decay upon the yield by comparing Nos. 12, 17 and 18, all of which are sound specimens, with Nos. 3, 4, 5 and 6; the annual ring growths compare

averages about 48 or 75 per cent, showing that the voids in 2 feet wood are less than in 4 feet wood. Comparing the solid cubic feet we find it to be about 100 in the case of 2 feet wood and 95 in 4 feet wood.

From experiments not shown here, it has been proven that large wood contains more solid wood per cord than small sizes, in the ratio of about 96 to 92.

From these results it is apparent how important it is to the manufacturer of chemical pulp to know

TABLE I—MONTMORENCY WOOD TEST (NOVEMBER, 1912)

No	DESCRIPTION OF SAMPLE	Diameter	Rings per inch	Sp. gr. of wood dried at 100° C.	YIELD		
					Per cent by weight	Per cent by volume	Lbs. per cord
2 Ft. Wood—100.3 SOLID FT. PER CORD							
1	Sound, fine grain	10"	23.3	0.4700	51.6	24.2	1515
2	Sound, fine grain	7	21.4	0.3522	51.5	18.1	1132
3	Dead wood, medium coarse	8 1/2	14.1	0.3697	49.5	18.3	1144
4	5" of center dry rot well established	9	13.1	0.3535	47.2	16.7	1045
5	4" of center dry rot, poor	10	15.6	0.3518	52.3	18.5	1157
6	4" of center dry rot, very poor	8	15.4	0.3474	48.2	16.7	1045
7	Fine grain, slight indication of dry rot surface	8 1/2	24.4	0.4141	52.8	21.9	1370
8	Sound	8	19.2	0.3076	53.5	16.4	1026
9	Sound, very coarse grain	7	6.8	0.3475	55.2	19.0	1189
10	Coarse grain, slight indication of dry rot surface	10	10.7	0.3565	54.1	18.2	1139
11	Sound	7 1/2	12.7	0.3242	53.9	17.5	1095
12	Coarse grain, sound	5	16.2	0.3166	52.1	16.4	1032
13	Dry rot and dead throughout, poor	7	16.3	0.3469	41.6	14.4	901
14	Coarse grain, dry rot well established throughout	5 1/2	10.2	0.3242	47.2	15.3	957
15	Coarse grain, sound	8	12.0	0.4094	54.0	22.1	1383
16	Coarse grain, dead wormy	5	12.5	0.3347	49.2	16.5	1032
4 Ft. Wood—95.64 SOLID FT. PER CORD							
17	Medium fine grain, sound	5 1/2	15.3	0.4011	55.0	22.1	1383
18	Coarse irregular grain, dense, sound	8 1/2	12.9	0.4333	54.5	23.6	1477
19	Coarse grain, rather light, sound	7 1/2	12.0	0.3556	56.1	19.9	1245
20	Coarse grain, sound	9	12.0	0.4291	57.2	24.5	1533
21	Fine grain, sound	7 1/2	19.7	0.3597	53.0	19.1	1195
22	Irregular grain, medium dense, sound	7	18.2	0.3651	51.6	18.8	1177
23	Very fine grain, dense, sound	10 1/2	24.0	0.3391	57.5	19.5	1220
24	Very fine grain, light sound	6	23.0	0.3368	59.0	19.9	1245

favorably and yet the specific gravities and yields of the latter are noticeably low.

III—The most important conclusion of all and the one we are perfectly safe in drawing is that there is great variation in the yield of chemical pulp and that some consideration should be given to this yield in fiber in valuing wood for pulp.

The yield per cord is found by taking the solid volume which the author has found to be about 100 cu. ft. and multiplying by the specific gravity. This gives the cord weight basis from which the yield in fiber can be calculated.

The volume yield is found by multiplying the specific gravity into the percentage fiber yield. The specific gravity of wood is very quickly determined approximately by displacement in mercury instead of water.

TABLE II—MONTMORENCY WOOD TEST (NOVEMBER, 1912)

Moisture per cent	Weight of one cord Lbs.		Area in one cord		Volume in one cord		No. of sticks in one cord
	Wet	Dry	Actual sq. ft.	Per cent total	Actual cu. ft.	Per cent total	
2 Ft. Wood							
40.1	3990	2392	...	...	...	...	...
43.3	3992	2220	...	...	...	...	...
38.4	3636	2240	49.4	77.2	98.8	77.2	178
38.4	3616	2228	48.5	74.8	97.0	74.8	185
48.7	4395	2140	51.65	80.8	103.3	80.8	210
48.7	4255	2075	51.15	79.8	102.3	79.8	184
4 Ft. Wood							
24.44	3014	2277	24.22	75.70	96.88	75.70	80
31.00	3313	2286	23.60	73.75	94.40	73.75	109

Table II shows the weights per cord of mixed spruce and balsam fir containing different percentages of moisture and the dry weight, which averages about 2200 lbs., free from moisture.

Comparing the square foot cross-section of a cord of 2 feet and 4 feet woods, we observe that the former averages about 50, or 78 per cent, while the latter

what his wood will yield and for his purposes it should be valued accordingly. Progress in valuing wood in any other way than by the cord unit will be slow, because all timber having a dimension lumber value will necessarily be valued by dimension. Again, as wood finds various markets, it will be valued according to the use it is put to in the highest market and the tendency to value all wood by the unit measurement of the principal market will persist. Meanwhile conditions are rapidly changing whereby the poorer grades of wood only are finding their way to the pulp mills and the question of supply and demand are determining factors.

So far as the author knows, manufacturers of pulp have done little or nothing to promote a better standard of valuing wood for their uses and we may expect no change until they take this matter more seriously in the interest of more efficient management of their plants.

RUMFORD, MAINE

## DETERMINATION OF CARBON IN SOILS AND SOIL EXTRACTS

By J. W. AMES AND E. W. GAITHER

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The method of estimating total carbon in soils by oxidation with a mixture of chromic and sulfuric acids has been tested by different chemists with varying results. Warrington and Peake<sup>1</sup> found that the chromic acid method gave lower results than those obtained by combustion in current of oxygen. Later, Cameron and Breazeale<sup>2</sup> compared the chromic acid

<sup>1</sup> Jour. Chem. Soc., 37 (1880), 617

<sup>2</sup> Jour. Am. Chem. Soc., 26, 29.



combustion with dry ignition in combustion furnace; the lower results obtained with chromic acid combustion as practiced by them, were no doubt due to the fact that the mixture was heated only until the sulfuric acid began to give off fumes. Hall and Miller<sup>1</sup> re-examined the method and concluded that the error was due to incomplete oxidation, other substances than carbon dioxide being produced. They found that by passing the products of combustion over heated copper oxide, all the carbon could be obtained as carbon dioxide. Their method calls for the addition of concentrated sulfuric acid and heating before chromic acid is added, which may account for the differences found.

Soil investigations in progress required the determination of carbon in 1 per cent hydrochloric acid and 4 per cent ammonia extracts of soils. Since neither the combustion furnace nor Parr apparatus<sup>2</sup> could be used on account of impracticability of reducing volume of solution to dry condition for combustion in boat or explosion bomb, the chromic acid combustion suggested itself as the most feasible method.

This led to a thorough test of the method for total carbon in soils, as compared with results obtained by combustion with copper oxide in furnace. The use of the Brown and Escombe double titration method for estimating carbonate in presence of sodium hydrate as suggested by Amos,<sup>3</sup> and a modification of his apparatus has contributed much to the successful operation of the chromic acid combustion as practiced in this work. The apparatus as modified by the junior author is shown in cut with accompanying explanatory details. It can be assembled on a single ring stand and requires only 16 inches table space. The absorption tube permits of a much smaller volume of 4 per cent solution of sodium hydroxide for absorption of carbon dioxide, thus reducing the blank and making it practicable to titrate the entire solution instead of an aliquot.

By adopting this procedure for determination of carbon dioxide rather than that of weighing an absorption bulb, the long purifying train is eliminated. The only substance likely to interfere with the titration would be hydrogen sulfide which could scarcely be evolved from such a strong oxidizing solution. This method was found to be applicable for estimation of carbon dioxide evolved from either the wet or dry combustion, and was used throughout the work here reported.

The soil samples selected for this work varied considerably as to their formation and content of inorganic and organic carbon.

#### DESCRIPTION OF SOILS

Lab. No.	Origin	Litmus reaction	Mineral carbon Marr method per cent
4655.....	Swamp clay	Very acid	0.000
4754.....	Limestone clay	Neutral	0.024
4755.....	Limestone clay	Very alk.	0.444
5577-1.....	Silt loam	Acid	0.000
1416-3.....	Prairie	Neutral	0.000

#### TOTAL CARBON

The following methods were employed for estimation of total carbon in soil.

<sup>1</sup> Jour. Chem. Soc., **89** (1906), 595.

<sup>2</sup> Jour. Am. Chem. Soc., **26**, 296 1640.

<sup>3</sup> Jour. Agr. Sci., **1**, Part 3, 322.

**1—IGNITION IN FURNACE WITH COPPER OXIDE—**From 1 to 3 grams of soil were thoroughly mixed in an agate mortar with five times its weight of copper oxide, transferred to porcelain boat and ignited in glass tube at bright red heat for 30 minutes, a current of CO<sub>2</sub> free air passing through tube carrying products of combustion over heated copper oxide during the whole time. The gas was turned off and air allowed to pass for 10 minutes. The carbon dioxide produced was absorbed in 25 cc. of 4 per cent sodium hydroxide made from sodium. When combustion was complete, the absorption solution was drawn out, the tower washed with 150 cc. carbon dioxide-free distilled water and the solution titrated by double titration, using phenolphthalein and methyl orange.

**2—COMBUSTION WITH CONCENTRATED CHROMIC AND SULFURIC ACID MIXTURE—**From 1 to 3 grams of soil were weighed into a 250 cc. short neck Kjeldahl nitrogen flask connected to apparatus; 10 cc. chromic acid solution containing 3.3 grams, then 50 cc. of concentrated sulfuric acid were run in through separatory funnel. This mixture was boiled 30 minutes, during which time a moderate current of carbon dioxide-free air was passed into the boiling mixture, sweeping out the carbon dioxide evolved, which was absorbed and titrated as under copper oxide combustion.

**COMBUSTION WITH DILUTE CHROMIC AND SULFURIC ACID MIXTURE—**The same as for concentrated chromic acid except that 50 cc. of water were added before the chromic and sulfuric acids.

**3—COMBUSTION WITH ALKALINE PERMANGANATE—**From 1 to 3 grams of soil were placed in 250 cc. Kjeldahl flask, 100 cc. of a solution containing 8 grams sodium hydroxide and 5 grams potassium permanganate added; the flask connected to the apparatus and boiled for one hour; the mixture was cooled, the 4 per cent solution of hydroxide placed in absorbing tower and 50 cc. of one part sulfuric acid and two parts water run into flask through separatory funnel. After boiling 15 minutes, the carbon dioxide evolved was determined by titration.

TABLE I—TOTAL CARBON—COMPARISON OF RESULTS BY DIFFERENT METHODS

Lab. No.	1 Ignition in furnace with copper oxide	2 Com- bustion with conc. chromic acid	3 Com- bustion with diluted chromic acid	4 Alka- line KMnO <sub>4</sub> method	5 Combustion with conc. chromic acid pass- ing over heated copper oxide	Differences in results Column 1— Column 2
4655.....	4.446	4.442	4.152	3.780	4.428	—0.006
4754.....	3.553	3.600	3.324	3.282	3.552	—0.047
4755.....	3.654	3.672	3.430	3.180	3.660	—0.018
5577-1.....	1.226	1.152	1.068	1.063	1.156	0.074
1416-3.....	4.011	4.036	3.792	3.855	4.044	—0.025

It is seen from these results, that for soils, the continued boiling with concentrated chromic acid gives results agreeing with those by the ignition method, within the limits of experimental error, while if the mixture is dilute, the results are too low, and that the results obtained with alkaline permanganate are entirely too low throughout. To determine if the oxidation with chromic acid had been carried to a complete reaction giving carbon dioxide as the final product, the gases from combustion with concentrated chromic acid mixture were passed over heated copper oxide before being

absorbed. These results in Column 5 agree very closely with results obtained from combustion in furnace and with chromic acid mixture only (Columns 1 and 2).

In all cases where the digestion was made with the concentrated solution, the silicates of the soil were disintegrated and rendered gelatinous; upon dilution and filtering the digested residue, its bulk was found to be greatly increased. By rubbing in beaker with glass rod, very little grit was found to remain. On reigniting three or four of the residues in the furnace with copper oxide, no carbon dioxide was recovered. This seems to be conclusive proof that the concentrated chromic and sulfuric acid treatment<sup>1</sup> completely decomposes organic and inorganic carbon present in soils and overcomes the objection raised by Cameron and Breazeale, and Hall and Miller in their articles previously cited.

#### CARBON IN 4 PER CENT AMMONIUM HYDROXIDE SOIL EXTRACT

To determine whether or not moderate dilution prevented the complete oxidation of humus materials by this method, three duplicate 50 cc. portions of the Grandeau humus extract, equivalent to 1 gram of soil, were pipetted off; two sets were evaporated to dryness on steam bath, and transferred to the digestion flasks with three successive 5 cc. portions of 4 per cent ammonium hydroxide and 15 cc. of water. One of these sets was placed in water bath heated to 65° C., and distilled to dryness under reduced pressure, and carbon determined on the dry residue. Carbon was determined on the other two sets without concentration.

TABLE II—CARBON IN HUMUS SOLUTION BY CHROMIC ACID METHOD  
(Expressed as per cent of soil)

Lab. No.	In dry humus residue after evaporating and distilling	In humus evaporated to dryness and diluted to 30 cc.	On original solution not evaporated nor distilled
4655.....	2.292	2.328	2.448
4754.....	2.088	2.160	2.172
4755.....	1.620	1.536	1.848
5577-1.....	0.720	0.696	0.672
1416-3.....	2.532	2.316	2.712
Average.....	1.850	1.807	1.970

The results in Columns 1 and 2 are within the limits of experimental error and show that 30 cc. dilution does not prevent the oxidation of humus substances. The difference between the averages of Columns 1 and 2, and Column 3 can be accounted for by the loss of volatile and easily oxidizable carbonaceous matter through evaporation on the steam bath. It is evident that moderate dilution does not prevent the oxidation of humus by chromic acid after it has been extracted from the soil by 4 per cent ammonium hydroxide. If all of the HCl is not washed from the soil before extracting with 4 per cent ammonium hydroxide, a trace of Cl may come over and be absorbed. This may be corrected by the addition of 1/2 cc. 10 per cent sodium thiosulfate or by introduction of a U-tube containing silver sulfate between the digestion flask and absorption tower.

<sup>1</sup> Adding the CrO<sub>3</sub> before adding H<sub>2</sub>SO<sub>4</sub> gives an oxidizing solution before the organic matter is charred by H<sub>2</sub>SO<sub>4</sub>.

#### CARBON IN 1 PER CENT HYDROCHLORIC ACID SOIL EXTRACT

At first this determination presented some difficulties. All of the chlorine and chromium chloride were not condensed in the reflux condenser, but a portion was carried over and absorbed with the CO<sub>2</sub>. This destroyed the indicators. This defect was overcome by the addition of 4 cc. of a 10 per cent solution of sodium thiosulfate just before titrating. This gave a clear, sharp end point with both indicators, and no further trouble was experienced in obtaining good duplicates.

The volume of hydrochloric acid extract used was concentrated to about 30 cc. by distilling under reduced pressure before adding the chromic and sulfuric acids.

In order to test the accuracy of the methods, a set of soils, 5 grams each, were extracted with 1 per cent HCl, then with 4 per cent ammonium hydroxide according to official method of the A. O. A. C., *Bulletin* 107, revised, Bureau of Chem., U. S. D. A.

Instead of using Gooch crucibles with asbestos mat, an alundum crucible was used, eliminating the asbestos. The 1 per cent hydrochloric acid extract and washings were made to a volume of 500 cc. Nine-tenths of the 4 per cent ammonium hydroxide solution was siphoned off, disturbing the settled soil as little as possible, leaving the residue from 5 grams of soil and one-tenth of the 4 per cent ammonium hydroxide extract. This was transferred to beakers, evaporated, dried, ground in an agate mortar and weighed. One-fifth of this was weighed into the digestion flasks, carbon determined, and results calculated to per cent of carbon on basis of original soil, allowing for the carbon in the 4 per cent ammonium hydroxide. Carbon was determined on the 1 per cent HCl and 4 per cent NH<sub>4</sub>OH extracts, and the mineral carbon was determined by the Marr method.<sup>1</sup> The sum of these fractions should equal the total carbon found in the soil.

TABLE III—COMPARISON OF SUM OF FRACTIONAL DETERMINATION OF CARBON IN SOILS WITH THE TOTAL CARBON

Lab. No.	Mineral	Organic in 1 per cent HCl extract	In 4 per cent NH <sub>4</sub> OH extract	In soil residue after extraction	Sum of fractions	Total by dry ignition in furnace	Total by combustion with chromic acid
4655.....	0.000	0.384	2.532	1.391	4.307	4.445	4.452
4754.....	0.026	0.252	2.220	1.110	3.608	3.538	3.600
4755.....	0.444	0.180	1.860	1.194	3.678	3.654	3.672
5577-1.....	0.000	0.136	0.600	0.456	1.192	1.226	1.152
1416-3.....	0.000	0.396	2.568	1.051	4.015	3.996	4.036
Av.....	...	...	...	...	3.320	3.375	3.382

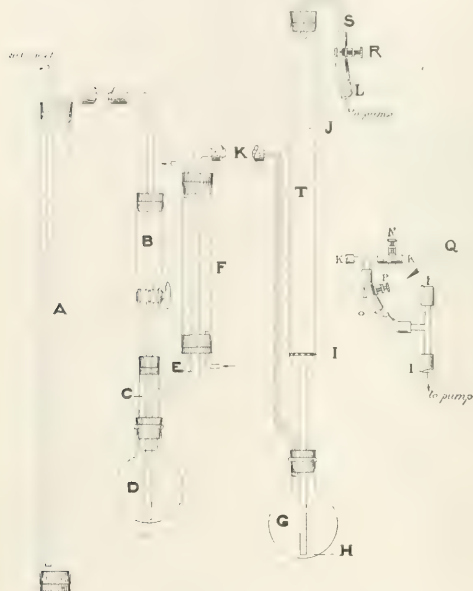
It is seen from these results that the average differences between the total carbon determined direct, and the sum of the fractions are well within the limits of experimental error, and that the method as applied to soil extracts is reliable and accurate. In all the work here reported, every fifth determination was a blank made under exactly the same conditions as the determinations so that the necessary correction could be made.

#### OPERATION OF APPARATUS

If it is desired to free the apparatus from CO<sub>2</sub>

<sup>1</sup> *Jour. Agr. Sci.*, 3, Part 2, 155.

before starting a determination, the arrangement shown at *Q* may be inserted, glass "*T*" *k k* at *K* and glass "*T*" *l l* at *L*, connected by tube *O*. By closing *N* and *R* and opening *P*, the  $\text{CO}_2$  may be removed from *D*, or by connecting *S* with a tower similar to



*A* and leaving *N* and *P* open, closing *R*, the whole apparatus may be freed from  $\text{CO}_2$ . This is usually unnecessary since the blank takes care of the  $\text{CO}_2$  that is in the apparatus.

The sample is placed in *D* which is connected to *C*. The absorbing liquid is placed in *G* and this connected to tower *T*. The stopcock in *B* is closed and digesting liquid placed in *B* which is then connected to *A*. Water is started through condenser *F* and the suction started. *R* is slowly opened until the liquid in *G* is drawn into *T* and a moderate flow of air started. The stopcock in *B* is opened and the digesting liquid run into *D*, using ordinary care. When air begins to flow from *A*, the heat is applied to *D* and the process continued to completion. When this point is reached, remove flame, close *R*, disconnect *B*, then *G*, and remove stopper from tower *T*. Receive content of *T* in *G* and wash out *T* with 100 cc. of  $\text{CO}_2$ -free water, using successive 25 cc. portions and titrate content of *G*.

The tower *A* and apparatus *T-G* may be used for the determination of carbon by ignition in a furnace, without the use of the customary purifying train.

This form of apparatus is less expensive, more easily operated, and just as efficient as the one shown in THIS JOURNAL, 4, 612.

#### CONCLUSIONS

If boiled for 30 minutes, a mixture of 3.3 grams of chromic acid in 10 cc. of water to 50 cc. of sulfuric acid (sp. gr. 1.84) will oxidize all of the organic carbon

and liberate all carbon dioxide chemically or mechanically held in soils, provided the soil is ground to pass 60 mesh sieve and from 1 to 3 grams of soil used for each 60 cc. of mixture.

If the mixture is diluted with 50 cc. of water, the results obtained are too low.

The alkaline permanganate method gives too low results.

The Brown and Escombe titration method of determining carbon dioxide, and the modified Amos absorption tower for same, are applicable to either wet or dry combustion forms of apparatus, and can be relied upon to give rapid and accurate results with considerable economy of time and space.

Carbon may be accurately determined in 1 per cent hydrochloric acid extracts and 4 per cent ammonium hydroxide humus solutions without concentrating below 50 cc. by using the above chromic and sulfuric acid mixture.

The apparatus described is applicable to the determination of carbon dioxide in any form, and a number of other gas determinations, depending on absorption in acid or alkalis, oxidation or reduction processes.

By using the apparatus shown in the cut, and following the method as outlined, one analyst can run six determinations at one time, and complete a set an hour when doing routine work, making it possible to run forty-eight total carbons in an eight-hour day.

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### THE MELTING AND SOLIDIFYING POINTS OF MIXTURES OF FATTY ACIDS AND THE USE OF THESE POINTS TO DETERMINE THE COMPOSITION OF SUCH MIXTURES

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The tables of melting points of mixtures of lauric, myristic, palmitic and stearic acids by Heintz<sup>1</sup> show certain regularities which Heintz himself noted, and which are referred to by Ostwald in his "Lehrbuch der Allgemeinen Chemie," 2d Ed., Vol. I, p. 1017, where he observes that it matters little which of these fatty acids of a lower melting point is added, in a certain proportion up to 40 per cent, to one of a higher, the lowering of the melting point of the latter is almost the same; also any of the fatty acids of higher melting point may be added to one of a lower (in definite proportion up to 15 or 20 per cent) and will cause the same depression. In other words, any of the fatty acids examined, when added in a certain proportion up to 20 per cent to any other, will cause a lowering of the melting point of the solvent acid depending on the amount of the acid added but independent of its kind.

This fact he explains by the law of equal depression of the freezing point for equal molecular proportions. This explanation assumes that the different fatty acids considered have the same molecular weights, which is, of course, not true, but the molecular weight of these fatty acids, and in fact of the fatty acids found in most

<sup>1</sup> Poggendorff's Annalen, 92, p. 588.



fats, are near enough together to allow of this assumption being made for the purposes of the calculations which I shall describe in this paper.

The following research was undertaken with the idea of reversing the usual process and, instead of using the lowering of the freezing point to calculate the molecular weight, to consider the molecular weights as known and determine the quantity of the dissolved fatty acid from the lowering of the freezing or melting point. For instance 20 per cent of an unknown mixture of fatty acids might be added to pure stearic acid and would produce a known depression of its solidifying or melting point, provided the fatty acid mixture contained no stearic acid; but if it did contain stearic acid the depression would be less and the percentage of stearic acid in the mixture could be calculated. Also the other components of the mixture could be determined by mixing with the corresponding pure fatty acids.

The method of identifying a pure substance with another by mixing the two together and noting whether there is a change in the melting point, is a particular case of this method and especially adapted to the examination of the solid fatty acids of natural fats, as the fatty acid to be identified need not be entirely free from other acids. If the change in melting point is less than a certain amount, the substance can be considered for the most part identical with the acid with which it is mixed.

Heintz's tables are evidently melting-point tables. Very careful measurements of the solidifying points of pure stearic and palmitic acid and of mixtures of the two have been made by DeVisser.<sup>1</sup> Some of these I shall refer to in comparison with the results of the following work, the object of which was to prepare various pure fatty acids and to determine the solidifying and melting points of their mixtures in various proportions, and to apply these values to the analysis of fatty acid mixtures on the principle I have described.

I have so far prepared three fatty acids, stearic, palmitic and behenic acid, in a fairly pure state.

The stearic acid was obtained from "hydrogenated" corn oil, that is, corn oil which had been saturated with hydrogen in the presence of nickel powder by Sabatier and Senderen's catalytic process. The fatty acids from this were distilled in a current of superheated steam and the last fraction crystallized a number of times from petroleum ether and from alcohol. This stearic acid had a solidifying point of 69.04° and a melting point in a capillary tube of 69.30°. Its combining weight, by titration with alkali, was 284. It was not quite pure as the last crystallization still caused a slight increase of the solidifying point. I am inclined to believe that the solidifying point, given by DeVisser, of 69.32 is near the correct one, and if so, my stearic acid would contain about 1.2 per cent of impurity.

The palmitic acid was obtained from myrtle wax, the fatty acids of which were distilled and then crystallized several times from petroleum ether and then from alcohol. This had a solidifying point of 62.14

and a melting point of 62.44. Its combining weight was 255.3. If DeVisser's figure, 62.618, is correct for the solidifying point of palmitic acid, my sample would have about 1.4 per cent of impurity.

The behenic acid was obtained from hydrogenated menhaden oil, the fatty acids of which were distilled and the last fractions crystallized ten times alternately from petroleum ether and alcohol. It had a solidifying point of 79.59° and a melting point of 79.99°. Its combining weight was 340.9.

All these fatty acids were resaponified to decompose any ethyl esters which might have formed in crystallizing from alcohol.

I also prepared oleic acid free from solid fatty acids (but not entirely free from other acids) by dissolving 20 g. of commercial oleic acid of good cold test (9° C.) in 250 cc. of 95 per cent hot alcohol and adding 1.2 grams of lead acetate also dissolved in 100 cc. of hot alcohol; then cooling to 10° C. The precipitate was filtered off and the filtrate treated in the usual way to extract unsaponifiable matters. The oleic acid recovered had an iodine value of 92.96.

The solidifying points of the following tables were obtained in the Beckmann apparatus for determining molecular weights by the freezing-point method, using 20 grams of material. The outer vessel contained water which was heated to the desired temperature by a small flame. I found, however, that in most cases, the same results were obtained by simply air-jacketing the tube as is done in the ordinary "titer test," except that if, instead of the platinum wire, the thermometer itself was used as a stirrer, my results were always about 0.15° too low. A Jena normal glass thermometer was used and corrections were made for the mercury column projecting above the tube.

Table III will not be discussed in this paper. The first double column of Tables I and II gives De Visser's figures. Comparing the first and second double columns of both tables it is seen that though my solidifying points of both stearic and palmitic acids are lower than those given by De Visser (which I admit may be due to impurities in my preparations), the depression caused by the addition of the other acid is about the same; that is, the impurity of the solvent does not affect the lowering of the solidifying point. This is further shown by the figures of the fourth column. The solidifying point of 80 parts of stearic acid plus 10 of palmitic acid plus 10 of oleic acid, as shown in the table, is 64.71°. As the solidifying point of 80 parts of stearic acid plus 10 of palmitic acid, calculated by interpolation in the table, is 66.52, the depression caused by adding 10 parts of oleic acid to a mixture of 80 stearic plus 10 palmitic acid is 66.52—64.71 = 1.81 or practically the same as that produced by adding 10 parts of oleic acid to 90 parts of pure stearic acid.

In the same way the solidifying point of 80 parts of stearic acid plus 10 parts of oleic acid is calculated as 67.03 and the depression caused by adding 10 parts of palmitic acid to this mixture is 67.03—64.71 = 2.32, about the same as by adding 10 parts of palmitic acid to 90 of pure stearic acid.

<sup>1</sup> Rec. trav. chim. Pays-Bas, 17, pp. 182-9.

TABLE I

	PALMITIC ACID DE VISSER		PALMITIC ACID		OLEIC ACID		EQUAL PARTS PAL- MITIC AND OLEIC		BEHENIC ACID	
	Solidif. pt.	Lowering of s. p. of solvent	Solidif. pt.	Lowering of s. p. of solvent	Solidif. pt.	Lowering of s. p. of solvent	Solidif. pt.	Lowering of s. p. of solvent	Solidif. pt.	Lowering of s. p. of solvent
STEARIC ACID.....	69.32	.....	69.04	.....	69.04	.....	69.04	.....	69.04	.....
95% stearic acid + 5% acid at head of column.....	.....	2.30	66.80	2.24	67.24	1.80	.....	.....	66.80	2.24
90% stearic acid + 10% acid at head of column.....	67.02	.....	64.29	4.75	65.35	3.69	64.71	4.33	65.26	3.78
80% stearic acid + 20% acid at head of column.....	64.51	4.81	.....	.....	.....	.....	.....	.....	.....	.....

TABLE II

	STEARIC ACID DE VISSER		STEARIC ACID		OLEIC ACID		EQUAL PARTS STEARIC AND OLEIC		BEHENIC ACID	
	Solidif. pt.	Lowering of s. p. of solvent	Solidif. pt.	Lowering of s. p. of solvent	Solidif. pt.	Lowering of s. p. of solvent	Solidif. pt.	Lowering of s. p. of solvent	Solidif. pt.	Lowering of s. p. of solvent
PALMITIC ACID.....	62.618	.....	62.14	.....	62.14	.....	62.14	.....	62.14	.....
95% palmitic acid + 5% acid at head of column.....	.....	3.308	59.01	3.13	60.30	1.84	.....	.....	59.58	2.56
90% palmitic acid + 10% acid at head of column.....	59.31	.....	56.13	6.01	58.30	3.84	56.80	5.34	58.26	3.88
80% palmitic acid + 20% acid at head of column.....	56.53	6.088	.....	.....	.....	.....	.....	.....	.....	.....

TABLE III

	Solidifying point	
1 50 parts stearic acid + 50 parts palmitic acid.....	56.09	
2 45 parts stearic acid + 45 parts palmitic acid + 10 parts oleic acid.....	54.31	Lowering of solidifying point of (1)..... 1.78
3 40 parts stearic acid + 40 parts palmitic acid + 20 parts oleic acid.....	54.47	Lowering of solidifying point of stearic acid..... 14.57
4 40 parts palmitic acid + 60 parts oleic acid.....	46.19	Lowering of solidifying point of palmitic acid..... 15.95
5 20 parts stearic acid + 20 parts palmitic acid + 60 parts oleic acid.....	41.70	Lowering of solidifying point of (1)..... 14.39

The solidifying point of a mixture of 80 parts of palmitic acid plus 10 of stearic acid plus 10 of oleic acid, as shown in this table, is 56.80. The solidifying point of 80 palmitic acid plus 10 stearic acid is calculated from the table as 58.68 and therefore the depression on adding 10 parts of oleic acid is 58.68—56.80 = 1.88. The solidifying point of 80 palmitic acid plus 10 oleic acid is calculated as 60.08 and therefore the depression on adding 10 parts of stearic acid is 60.08—56.80 = 3.28. These two values of the lowering of the solidifying point are about the same as those given in the table when the solvent is nearly pure.

The tables also show that the lowering of the solidifying point caused by adding oleic acid to one of the solid acids is much less than that caused by adding palmitic, stearic, or behenic acids. In fact the acids of highest solidifying points produce the greatest lowering of the solidifying point of the solvent. The lowering caused by oleic acid seems to be the normal one—that due to its molecular weight—corresponding to the factors for cryoscopic determinations of molecular weights with the solvents palmitic and stearic acid found by Eijkmann and others. Of course, in the above tables the dissolved acid is in much larger proportion than would be used in molecular-weight determinations.

The abnormal lowering of the solidifying point caused by stearic, palmitic and behenic acids seems to be due to the very great undercooling which it seems impossible to avoid. In some cases after crystallization begins the thermometer will rise nearly one degree before coming to a maximum.

If, after the solidifying point has been noted, the outer vessel containing water is very slowly heated and the fatty acid in the tube continually stirred until it melts completely, and this point is noted, it will be found that this point has no definite relation to the solidifying point before found, but is nearly the same for equal parts of various dissolved acids, as is shown in Table IV.

It is plain that the lowering of the solidifying point of a pure fatty acid caused by adding different members of the group of fatty acids examined varies too much

with the particular acid to permit the use of this method for calculating the composition of an acid mixture.

The next experiments were, therefore, made to discover whether measurements of melting points by the

TABLE IV

	Solidifying point	Reheated till clear
1 90% stearic acid + 10% behenic acid.....	65.26	67.66
2 90% stearic acid + 10% palmitic acid.....	66.81	67.46
3 90% stearic acid + 10% oleic acid.....	67.25	67.58
4 80% stearic acid + 20% palmitic acid.....	64.38	65.39
5 80% stearic acid + 20% oleic acid.....	65.38	65.80

capillary tube method would give results corresponding more closely to the freezing-point depressions required by theory.

This measurement is not so exact as that of the solidifying point and it requires some practice to get agreeing results; however, it has a great advantage in that only small quantities of substance are needed.

My method was as follows: A capillary tube with an internal diameter of between 0.5 and 1 mm., open at both ends, was warmed and one end dipped in the melted fatty acid mixture. The tube was then inverted and, with a violent jar, the material in the tube was broken up into a number of short columns which solidified. The tube was attached to the bulb of a thermometer which was suspended through a cork in an air bath formed by a test tube of about 3 cm. diameter; this test tube was immersed in a large beaker of water. Another thermometer was immersed in the water. With the help of this outer thermometer, the temperature of the water was so regulated that the thermometer with the capillary tube attached rose not faster than  $1/10^{\circ}$  per minute when the temperature reached the neighborhood of the melting point of the fatty acid. The point taken was that at which small columns showed decided clear portions. This should happen to all the small columns at nearly the same time. As before, corrections were made for the thermometer stem projecting above the tube.

If Tables V and VI are compared with Tables I and II it will be seen that the lowering of the solidifying point of the acid taken as the solvent depends much on the particular acid added, while this is not the case with the melting point. For example, the solidifying

TABLE V

	PALMITIC ACID		OLEIC ACID		EQUAL PARTS PALMITIC AND OLEIC		BEHENIC ACID	
	Melting point	Lowering of m. p. of solvent	Melting point	Lowering of m. p. of solvent	Melting point	Lowering of m. p. of solvent	Melting point	Lowering of m. p. of solvent
STEARIC ACID.....	69.30	...	69.30	...	69.30	...	69.30	...
90% stearic acid + 10% acid at head of column.....	67.20	2.10	67.27	2.03	...	...	67.29	2.01
80% stearic acid + 20% acid at head of column.....	65.08	4.22	65.37	3.93	65.30	4.00	...	...

TABLE VI

	STEARIC ACID		OLEIC ACID		EQUAL PARTS STEARIC AND OLEIC		BEHENIC ACID	
	Melting point	Lowering of m. p. of solvent	Melting point	Lowering of m. p. of solvent	Melting point	Lowering of m. p. of solvent	Melting point	Lowering of m. p. of solvent
PALMITIC ACID.....	62.44	...	62.44	...	62.44	...	62.44	...
90% palmitic acid + 10% acid at head of column.....	60.36	2.08	60.27	2.17	...	...	60.53	1.91
80% palmitic acid + 20% acid at head of column.....	58.16	4.28	58.28	4.16	58.40	4.04	...	...

TABLE VII

	STEARIC ACID		PALMITIC ACID		OLEIC ACID	
	Melting point	Lowering of m. p. of solvent	Melting point	Lowering of m. p. of solvent	Melting point	Lowering of m. p. of solvent
BEHENIC ACID.....	79.99	...	79.99	...	79.99	...
80% behenic acid + 20% acid at head of column.....	75.81	4.18	75.45	4.54	75.71	4.28
60% behenic acid + 40% acid at head of column.....	71.04	8.95	70.72	9.27	...	...

point of 90 parts of stearic acid plus 10 parts of oleic acid is 67.24, that of 90 parts of stearic acid plus 10 parts of behenic acid is 65.26, while the melting points of these two mixtures are 67.27 and 67.29, respectively. In other words, the addition of behenic acid to stearic acid does not cause the same abnormal lowering of melting point that it does of solidifying point. Also the melting and solidifying points of mixtures of a solid fatty acid with oleic acid are not so far apart as is the case with other acids.

Approximately the lowering of the melting point of the solvent for 10 and 20 per cent of dissolved acid is the same for all the acids examined. What variation there is can, to some extent, be attributed to the differences in molecular weights of the dissolved acids; but the present measurements are hardly accurate enough

The solid fatty acids were separated from the above acids as follows: To 20 grams of the fatty acids dissolved in 250 cc. of hot 95 per cent alcohol were added 4 grams of lead acetate in 100 cc. of the same alcohol. The liquid was allowed to cool and then stood overnight at a temperature of 10° to 15° C. The precipitate was filtered off, washed with a little alcohol and then boiled and washed with ether. The fatty acids were separated from the lead soap and had an iodine value of 3.00, corresponding to 3.3 per cent of oleic acid. Their mean combining weight was 258.7. The cottonseed oil fatty acids yield about 25 per cent of these solid acids.

The fatty acids separated from the oil which had been saturated with hydrogen had an iodine value of 1.80, equivalent to 2.0 per cent of oleic acid, which it

TABLE VIII

	<i>a</i> Melting point	<i>b</i> Lowering of m. p. of solvent	<i>c</i> Lowering of m. p. of solvent by 20% oleic acid		<i>d</i> 20 <i>b/c</i>	Stearic acid Per cent	Palmitic acid Per cent
1 80% stearic acid + 20% fatty acids of cottonseed oil.....	65.48	3.82	3.93	19.44	2.8	...	...
2 80% palmitic acid + 20% fatty acids of cottonseed oil.....	59.26	3.18	4.16	15.29	...	23.6	...
3 73% palmitic acid + 27% fatty acids of cottonseed oil.....	58.28	4.16	4.16	20.00	...	25.9	...
4 Solid fatty acids of cottonseed oil.....	59.35	3.09	4.16	14.85	...	85.2	...
5 80% stearic acid + 20% solid fatty acids of cottonseed oil.....	65.49	3.81	3.93	19.39	3.0	...	...
6 Hydrogenated cottonseed oil fatty acids.....	63.34	5.96	3.93	30.33	69.7	...	...
7 33 1/3% stearic acid + 66 2/3% of above acids.....	65.47	3.83	3.93	19.49	70.8	...	...
8 73% palmitic acid + 27% of above acids.....	58.10	4.34	4.16	20.86	...	22.7	...

to take into account these differences. However, they are sufficiently accurate to obtain a quite close estimate of the composition of a mixture of fatty acids.

As examples, I shall give the investigations of the composition of the fatty acids of samples of refined cotton seed and menhaden oil.

I examined not only the fatty acids of the oils, but the solid fatty acids separated from these by the lead soap ether method, and also the fatty acids from the oils after they had been "hydrogenated" or saturated with hydrogen.

#### THE FATTY ACIDS OF COTTONSEED OIL

The cottonseed oil fatty acids had a solidifying point of 35.24°. They contained 0.61 per cent of unsaponifiable matter. Their mean combining weight by titration with alkali, allowing for the unsaponifiable matter, was 276.

may be assumed to be, as it is not likely that there was much of the other unsaturated fatty acids in this residue.

The following table gives the melting points of mixtures of these three fatty acids with pure stearic and palmitic acid:

Column *b* gives the lowering of the melting point of the solvent acid by the acid mixture under examination. For mixture 1, it is the lowering of the melting point of stearic acid by adding to 80 parts of stearic acid 20 parts of cottonseed oil fatty acids.

Column *c* is the lowering of the melting point of the solvent acid, by 20 per cent (of the whole mixture) of oleic acid, or any acid other than the solvent. I have taken my values for oleic acid to represent the others as its molecular weight is about a mean of those of the acids examined, and it is not itself used as a solvent.



Column *d*, =  $20b/c$ , shows the percentage of dissolved acids in the mixture of solvent plus dissolved acids on the assumption that the melting-point curves are straight lines, which is very nearly true, but to avoid this possible error I have made mixtures, as 3, 7 and 8, so that *b* would be about the same as *c* and therefore *d* would equal 20.

To calculate the stearic or palmitic acid in the fatty acids added, deduct the figure in column *d* from the amount added and divide by the amount added.

Mixtures 1 and 3 show cottonseed oil fatty acids to contain 2.8 per cent of stearic acid and 25.9 per cent of palmitic acid. Mixtures 4 and 5 show the solid acids of cottonseed oil to contain 85.2 per cent of palmitic acid and 3 per cent of stearic acid. If there were really 2.8 per cent of stearic acid in the original acids, this should all be in the solid fatty acids separated and these should test higher in stearic acid; besides, the accuracy of the method is hardly great enough to assume the presence of stearic acid from a difference of melting point of only  $0.11^\circ$ . It will, therefore, be necessary to fractionate the solid fatty acids of cottonseed oil and obtain a fraction which, when added to stearic acid, will cause less lowering of its melting point than the amount given above before it can be said that stearic acid is present.

TABLE IX

		<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>			
		Melting point	Lowering of m. p. of solvent	Lowering of m. p. of solvent by 20% oleic acid	20 <i>b/c</i>	Stearic acid	Palmitic acid	Behenic acid
						Per cent	Per cent	Per cent
1	80% stearic acid + 20% fatty acids of menhaden oil.....	65.60	3.70	3.93	18.83	5.8	.....	.....
2	72% palmitic acid + 28% fatty acids of menhaden oil.....	57.91	4.53	4.16	21.78	.....	22.2	.....
3	80% stearic acid + 20% solid fatty acids of menhaden oil.....	65.45	3.85	3.93	19.59	2.0	.....	.....
4	80% palmitic acid + 20% solid fatty acids of menhaden oil.....	60.87	1.57	4.16	7.55	.....	62.2	.....
5	50% palmitic acid + 50% solid fatty acids of menhaden oil.....	58.36	4.08	4.16	19.63	.....	60.7	.....
6	80% behenic acid + 20% solid fatty acids of menhaden oil.....	75.43	2.31	4.16	21.31	.....	.....	.....
7	80% stearic acid + 20% fatty acids of hydrogenated menhaden oil.....	66.31	2.99	3.93	15.22	23.9	.....	.....
8	73% stearic acid + 27% fatty acids of hydrogenated menhaden oil.....	65.37	3.93	3.93	20.00	25.9	.....	.....
9	80% palmitic acid + 20% fatty acids of hydrogenated menhaden oil.....	59.35	3.09	4.16	14.86	.....	25.7	.....
10	72% palmitic acid + 28% fatty acids of hydrogenated menhaden oil.....	57.97	4.47	4.16	21.49	.....	23.2	.....
11	80% behenic acid + 20% fatty acids of hydrogenated menhaden oil.....	76.56	3.43	4.16	16.03	.....	.....	19.7
12	75% behenic acid + 25% fatty acids of hydrogenated menhaden oil.....	75.64	4.35	4.28	20.32	.....	.....	18.7
				Lowering of m. p. of solvent by 40% stearic acid	40 <i>b/c</i>			
13	50% behenic acid + 50% fatty acids of hydrogenated menhaden oil.....	71.05	8.94	8.95	39.95	.....	.....	20.1

unsaturated acids with 18 and 22 carbon atoms, respectively.

The above results indicate a composition for menhaden oil fatty acids about as follows:

Palmitic acid (average of 2 and 10).....	22.7%
Other solid, saturated acids (calculated from 2, 10 and 5 and considering iodine value of solid acids).....	11.8
Unsaturated acids with 16 carbon atoms.....	None
Unsaturated acids with 18 carbon atoms (from 8, considering iodine value of hydrogenated acids).....	26.7
Unsaturated acids with 22 carbon atoms (from 12 and 18, considering iodine value of hydrogenated acids).....	20.2
Other unsaturated acids.....	18.6
	100.0

These fatty acids, therefore, probably contain about 18.6 per cent of another unsaturated acid with some other number of carbon atoms, and also 11.8 per cent of another saturated acid. Information as to these acids can probably be gained by making mixtures with pure myristic and arachidic acid, but these two acids I have not at present at hand.

The above results do not show whether the unsaturated fatty acid with 18 carbon atoms is oleic, linolic, linolenic, or clupanodonic acid, and to which of these series the acid with 22 carbon atoms belongs. To determine this it would be necessary to, at least partially, separate the unsaturated acids from each other and hydrogenate them separately.

The results of the examination of the two fatty acid mixtures given show what can be learned of the composition of such mixtures by this melting-point method, especially when, in addition to the original fatty acids, the solid fatty acids separated from them and the acids after saturation with hydrogen are also tested.

When working with the fatty acids of a natural fat, the accuracy of the results is somewhat disturbed by impurities, such as oxidation products of unsaturated fatty acids as I have mentioned above. This method could be applied to determine the percentage composition of mixtures of known fatty acids with certainly greater accuracy. In this case, the molecular weight of the acids should be taken into consideration.

WYOMING, OHIO

## THE SPECIFIC HEAT OF MILK AND MILK DERIVATIVES

By ARDEN R. JOHNSON AND B. W. HAMMER

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In a great many dairy processes where heat is used, the amount and intensity of the energy necessary to gain a certain end-product are very important. These factors are important not only because heat, like material commodities, is an item of expense, but also, because too great an intensity of temperature, or too prolonged an application, may cause serious chemical and physical changes in the substance worked with.

The amount of heat which it takes to raise unit weight of a substance unit temperature depends upon its chemical nature and upon its physical state.

The ratio between the number of calories required to raise a given weight of a substance through a given temperature interval, and the number required to raise the same weight of the standard substance through the same temperature interval is called the "specific heat" of the substance. Water is always the standard substance so that the specific heat of a substance is the

number of calories required to raise one gram or one pound one degree Centigrade or Fahrenheit, respectively.

The heat capacity of a substance is obviously its specific heat multiplied by the quantity of the substance.

The heat capacity of a system is the sum of the heat capacities of all the substances in the system.

It is particularly important to bear in mind that the specific heat of a substance is not the same at all temperatures, though for most substances the changes are not great so long as the substances remain in the same physical state. But for different substances, or for the same substance in different physico-chemical conditions, the specific heats are very different. This makes specific heat a very important factor when handling large quantities of any substance which must be raised or lowered in temperature, and especially when the time and cost elements enter.

Persons interested in milk and milk derivatives who have to deal with great quantities of these materials upon narrow margins, both financially and in the matter of temperature control, face the necessity of a knowledge of all factors of any considerable magnitude.

In pasteurizing it is desirable to know the amount of heat required to bring a definite amount of milk or cream from the temperature at which it has been delivered or held up to the temperature used in pasteurizing, as well as the amount of refrigeration required to cool the same material down to a temperature satisfactory for storage or for inoculation. Although the losses which constantly occur, and which depend on a number of factors, prevent the exact computation of the amount of heat or refrigeration through a knowledge of specific heats alone, still, the exact experimental values are of great importance in calculating the cost of pasteurization, particularly when large quantities of material are being handled. The increasing use of pasteurization, both in plants selling milk, and in plants manufacturing butter, or ice cream from pasteurized cream, makes the specific heat values of increasing importance. In calculating the cost of storing butter and hardening ice creams the respective specific heats are also essential.

Prof. M. Mortenson of the dairy section of the Iowa Agricultural Experiment Station has recently called attention to the importance of the specific heat of the mix in ice cream work. Aside from the question of cost of hardening, the specific heat of the mix is apparently of significance in its effect on the palate, the sherbets and low-fat ice creams with a higher specific heat seemingly tasting colder than ice creams carrying considerable fat and accordingly having a lower specific heat.

### APPARATUS DESIGNS

In the prosecution of the work on the specific heat of milk and its derivatives herein described, two designs of specific heat apparatus were evolved. In both the electric current is used for heating, but with one a variable voltage may be used, while with the other a very constant voltage is necessary.

In apparatus No. 1, for variable voltage, Fig. 1, the

outer insulating walls (1) of the apparatus consist of pressed cork, such as is used in the construction of refrigerators and thermostats. In the cylindrical cavity (2), which may be gouged out with a sharp paring knife, is the copper (or glass) calorimeter vessel

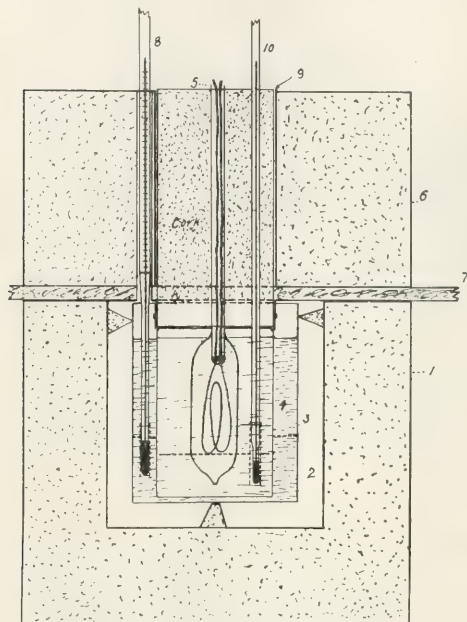


FIG. 1

(3) (diam. = 6.25 cm., height = 8.75 cm.) for holding 100 gms. of sample; (4) is another copper vessel (diam. = 4.7 cm., height = 8.1 cm.) with a capacity of 100 gms. of water in which is immersed an electric light bulb and a thermometer to which a stirrer is attached. The vessel is arranged with a tight-fitting cap having a bayonet catch. Leads from the electric lamp pass up through a fiber or glass tube (5) which also serves as a handle for the whole vessel and its contents which we may call the "heater." The upper portion (6) of the cork insulating vessel has cut through it a cylindrical hole just a trifle greater in diameter and deeper than the heater. Between the upper and lower portions of the cork container is a heavy asbestos board partition (7), the middle third of which is a slide that may be readily inserted or withdrawn.

#### OPERATION OF THE APPARATUS

The operation of the apparatus is as follows: 100 gms. of milk are weighed in the vessel (3) which is placed in the cork thermostat. A thermometer (8) reading to 0.1 degree C. is then inserted. The electric current is turned on the heater (4) and this allowed to come to a suitable temperature outside of the thermostat. If the temperature of the milk is 20 degrees C. it will be sufficient to heat the heater to about 45 degrees C. It is then placed in the cavity (9) and allowed to come to a condition such that radiation takes place

regularly, the thermometer (8) is read, and when the mercury of the thermometer (10) comes to a chosen mark, the heater is dropped down into the liquid in the calorimeter vessel. The liquids of both vessels are agitated regularly until the thermometer (8) shows the maximum rise of temperature. Results are obtained for water and the substance in hand for the same range of temperature. The specific heat of the substance is inversely proportional to the temperature rise, the rise being compared with that of water under like conditions. Corrections for radiation and the water equivalent of the calorimeter must, of course, be applied.

Apparatus No. 2 for constant voltage is shown in

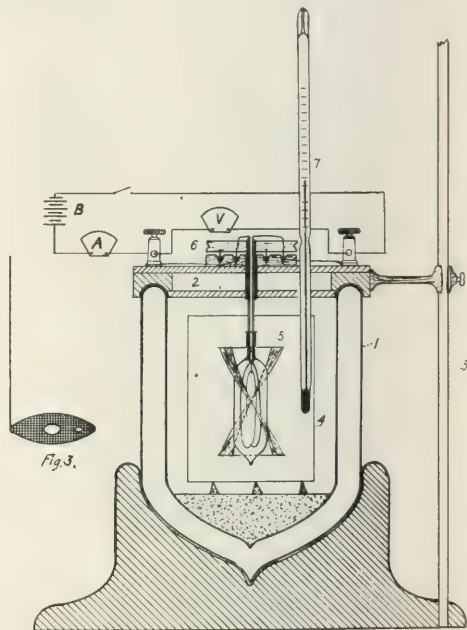


Fig. 3.

FIG. 2

Fig. 2, which is a cross-section drawing of a very satisfactory apparatus, not only for milk but for any liquid which is not appreciably volatile at ordinary temperatures. Part (1) is a Dewar flask supported in a wooden base and provided with a hollow wooden cover (2). This cover is attached to a clamp which slides up or down on the rod (3). From the cover of the vessel a small, narrow shank, 8 c. p. electric lamp projects down into the calorimeter vessel (4). The calorimeter vessel is made of thin copper or glass as desired, with a capacity of 500 cc. Smaller vessels may, of course, be used. The Dewar vessel should be about 12.5 cm. internal diameter and 15.0 cm. deep. The bottom is provided with a cork false bottom and small cork pyramids for the calorimeter to rest upon. A stirrer (5) in the form of a propeller may be clamped onto the lamp and the whole rotated by a motor belted to the pulley (6), or a reciprocating



stirrer may be provided. A good reciprocating stirrer of fine wire gauze soldered on two concentric wire rings is shown in Fig. 3. The two holes are for admitting the lamp and the thermometer. If a Dewar flask is not obtainable, a cork thermostat may be provided as shown in Fig. 4. Such a thermostat has been used by the authors and found to give very satisfactory

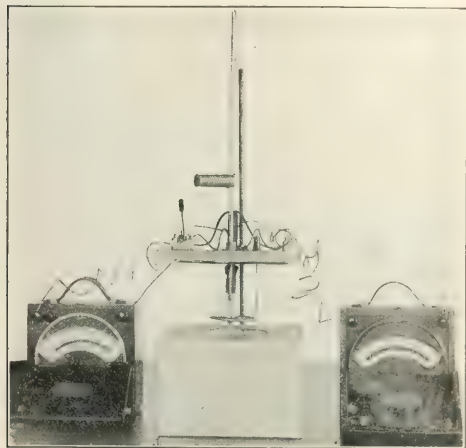


FIG. 4

results. As shown diagrammatically in Fig. 2, the lamp is connected in series with a storage battery, ammeter and switch. A voltmeter is placed across the lamp.

#### DETERMINING THE SPECIFIC HEAT

The specific heat of a liquid may be determined by either of two methods: a weighed sample of water is placed in the calorimeter, the temperature noted on the thermometer (7), the current turned on for say five minutes, and readings of the temperature taken every minute. (Stop-watch used.) The same procedure is then gone through for an equal weight of the substance whose specific heat is desired. Corrections for radiation are best obtained by allowing the apparatus to cool for the same length of time, within the same temperature range, as was devoted to the heating, and adding this value to the rise in temperature obtained by heating five minutes. If working below room temperature, there will be a gain in temperature, on standing five minutes with lamp off, which must be subtracted from the reading obtained by heating five minutes. The specific heat of the substance is then found by comparing its temperature rise with that of distilled water. (Equal weight.)

By the second method the respective amounts of electrical energy expended on the substance and water to raise them the same temperature may be compared by multiplying the drop across the lamp (voltage) in amperes into time and dividing by 4.26 to reduce to calories. If the source of electric energy gives a constant voltage, the first two terms, drop and amperage,

will be constant and we may compare the time terms only.

#### SPECIFIC HEAT OF WHOLE MILK

The samples of milk used in the tests were from the composite milk delivered at the College creamery. The fat content varied from 3.4% to 4.9%, most samples having about 4.3%. About 15 hours elapsed between the time the milk was drawn from the cows and the time of the tests. After the milk was delivered at the creamery the samples were kept in the refrigerator.

The averaged results for the various temperatures have been plotted in the form of a curve (see Fig. 5).

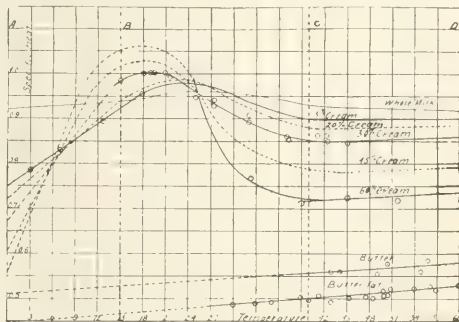


FIG. 5—CURVES SHOWING AVERAGED SPECIFIC HEATS OF WHOLE MILK AT VARIOUS TEMPERATURES

Though the changes in the specific heat of milk between 15.0° C. and 60.0° C. are not great, still there is shown, by our data, a fairly pronounced maximum at about 30.0° C. Some of the reasons for this will be discussed later.

#### SPECIFIC HEAT OF WHEY

The whey used was from composite milk and was obtained from the cheese vat. There was present from 0.25 to 0.30% fat and the samples were opalescent. The values obtained for two samples taken at different times were very near one another. The average specific heat between 23° and 33° C. was 0.975.

TABLE I—SPECIFIC HEAT OF WHEY

Sample No. 1		Sample No. 2	
Temp. range	Sp. heat	Temp. range	Sp. heat
22.99	0.977	22.93	0.977
28.38	0.974	28.32	0.973
33.60	0.974	33.85	0.973
Av., 0.975		Av., 0.975	

#### SPECIFIC HEAT OF SKIM MILK

Samples of sweet skim milk, varying in fat content from 0.30 to 0.38%, were obtained from a small separator immediately after running through the machine. The average of 15 determinations on 4 different samples made between approximately 20° and 40° C. gave an average value of 0.949. Over the pasteurizing range of 60°–70° C. the average value of 0.963 was obtained.

#### SPECIFIC HEATS OF CREAM

The creams used were sweet and were separated from

TABLE II—SPECIFIC HEAT OF SKIM MILK

Sample No. 1		Sample No. 2		Sample No. 3	
Temp. C.	Sp. h.	Temp. C.	Sp. h.	Temp. C.	Sp. h.
18.80		15.35		21.00	
	0.951		0.941		0.942
24.00		20.72		26.20	
	0.948		0.941		0.940
29.70		25.88		31.20	
	0.957		0.937		0.948
34.54		30.90		36.00	
	0.955		0.958		
39.32		35.70			
	0.957				
44.95					
	0.954		0.944		0.943
Average	0.954				
Sample No. 4		Sample No. 5		Sample No. 6	
Temp. C.	Sp. h.	Temp. C.	Sp. h.	Temp. C.	Sp. h.
20.30		61.90		58.55	
	0.946		0.977		0.942
25.80		65.58		62.55	
	0.960		0.974		0.948
31.09		68.20		65.20	
	0.957		0.972		0.952
36.14		70.60		68.10	
				70.66	
					0.966
Average	0.954		0.974		0.952

composite milk in the morning and kept in a refrigerator until evening, when the measurements were carried out. A series of determinations was made on each sample over quite a wide range and generally up to about 60° C.

In the course of the measurements on creams it was found that *apparent* specific heats considerably above 1.000 were often encountered. This peculiarity of cream was also noted by Fleischmann. The authors' data for 33.5 per cent, 30 per cent, 27 per cent, 15 per cent and 60 per cent creams have been obtained under very definite conditions and the results averaged; from the averages the curves shown in Fig. 5 have been plotted and these will be discussed later. The 60 per cent cream was first heated, as it was very viscous at room temperature.

#### SPECIFIC HEAT OF BUTTER

Three samples of butter taken from the churning on three different occasions, and containing the ordinary amounts of curd, salt, water and fat gave the following results:

TABLE III—SPECIFIC HEAT OF BUTTER

No.	Per cent salt	Per cent curd	Per cent water	Per cent fat	Av. sp. heat 30-60° C.
I...	2.2	0.60	14.20	83.0	0.688
II...	1.02	0.48	13.50	85.0	0.557
III...	1.14	0.76	13.60	84.5	0.574

The values for ordinary butter are considerably higher than for pure fat. This is in part due to the presence of considerable quantities of water.

#### SPECIFIC HEAT OF BUTTER FAT

Butter fat carefully prepared in accordance with the specifications of the official method gave the following results:

TABLE IV—SPECIFIC HEAT OF BUTTER FAT

No. 1. Average from 30°-60° C. equals 0.532
No. 2. Average from 30°-60° C. equals 0.510

Average, 0.521

Samples of practically pure butter fat were also prepared by taking freshly churned butter, placing it in a large separatory funnel, and keeping it in a thermostat at 43° C. so as to allow the fat, curd and water to separate by gravity. Water was added several times, shaken with the melted fat, and allowed to separate and then drawn off. Next fused calcium chloride was

added and the melted fat thoroughly dried, then filtered. The average value between 30° and 60° C. for four samples thus treated was 0.507. At 30° C. it was 0.485 and at 60° C. 0.530.

#### DISCUSSION OF RESULTS

A review of the literature on the work hitherto carried out by several investigators on the specific heats of milk, cream and butter reveals fairly close agreement in the results for the specific heat of milk, but for butter and cream the results of the same and different investigators are greatly at variance. In the case of creams there is no consistency whatever in the results. Fleischmann's results obtained with a very elaborate apparatus, and representing a vast amount of labor, cannot be put together so as to show consistent relationships between the specific heats and the variable factors of temperature, fat content, and physico-chemical conditions of creams.

To show that there are indeed definite relationships between the above factors, and co-ordination where at first appear only capricious results, we have plotted, in the form of curves, results obtained in the course of our experiments.

The curves on Fig. 5 show the values at various temperatures, for whole milk, creams containing different amounts of fat, butter, and butter fat. The solid lines represent results obtained experimentally while the dotted lines, except in the case of the 20 per cent and 45 per cent creams, represent values that it is impossible to obtain experimentally with our apparatus on account of the viscosity of the creams and the solidifying of the butter and butter fat at the lower temperatures. It will be seen that the values for 15 per cent cream have been obtained almost down to 0.0° C. and

TABLE V—SPECIFIC HEATS OF MILK AND MILK DERIVATIVES Including heat required to melt fat if this factor enters Values obtained from Curves, Plate V

	At 0° C.	At 15°	At 40°	At 60°
Whey.....	0.978	0.976	0.974	0.972
Skim milk.....	0.940	0.943	0.952	0.963
Whole milk.....	0.929	0.938	0.930	0.918
15 per cent cream.....	0.750	0.923	0.899	0.900
20 per cent cream.....	0.723	0.940	0.940	0.886
30 per cent cream.....	0.673	0.983	0.852	0.860
45 per cent cream.....	0.606	1.016	0.787	0.793
60 per cent cream.....	0.560	1.053	0.721	0.737
Butter.....	0.512a	0.556(a)	0.556	0.580
Butter fat.....	0.445a	0.467(a)	0.500	0.530

(a) These values were obtained by extrapolation, assuming that the specific heat is about the same in the solid and liquid states.

	AV. SP. HEATS					
	0°-15°	0°-40°	0°-60°	15°-40°	40°-60°	15°-60°
Whole milk...	0.929	0.940	0.935	0.947	0.923	0.937
15 per cent cream...	0.837	0.900	0.889	0.940	0.899	0.925
20 per cent cream...	0.811	0.894	0.890	0.936	0.881	0.916
30 per cent cream...	0.830	0.883	0.875	0.925	0.854	0.899
45 per cent cream...	0.832	0.866	0.843	0.901	0.786	0.858
60 per cent cream...	0.843	0.851	0.816	0.876	0.727	0.821
Butter.....					0.568	
Butter fat.....					0.514	

that the values for 30 per cent cream have been obtained down below 15.0°. The rises in the case of the 45 per cent and 60 per cent creams have been assumed to be proportional to the fat content and the same assumption has been made with regard to the fall of the various curves. The reason for constructing these curves on assumptions only is to make possible the compilation of the results given in Table V. Here-fore, it has been customary to use a certain value for the specific heat of milk or cream without paying any attention to the temperature range over which the

material is to be heated or cooled. This is obviously wrong because the range plays a very important part from the standpoint of the apparent specific heat value, and for that reason Table V was prepared, although it is recognized that certain of the values may be in error because of the assumptions that have been necessary. In addition to giving the values of certain temperatures the table gives the values over various ranges; these were obtained by averaging the values for every 3° C.

TABLE VI—SPECIFIC HEAT VALUES FOR MILK AND MILK DERIVATIVES  
Collected from the Dairy Literature

Material	Conditions		Investigator	Reference
	Temperature ° C.	Per cent fat    Specific heat		
Whole milk.....	16-17	10.9406	Chanoz and Vaillant	<i>Grimmer-Chemie und Physiologie der Milch</i> , Orig.
Whole milk.....	14-16	10.9523	Fleischmann	<i>Journ. de Phys. et de Pathol. generale</i> , 8, p. 413.
Whole milk.....	27.5 up to 40 and return	0.9457	Fleischmann	<i>Jour. Landwirtschaft</i> , 80, p. 33.
Whole milk.....	.....	0.9351	Fleischmann	<i>Jour. Landwirtschaft</i> , 80, p. 33.
Skim milk.....	14-16	0.94	Fjoid	McKay and Larsen, "Principles and Practices of Butter Making."
Skim milk.....	27.5 up to 40 and return	0.20    0.9388	Fleischmann	<i>Loc. cit.</i>
Skim milk.....	14-16	19.18    0.9455	Fleischmann	<i>Loc. cit.</i>
Cream.....	27.5 up to 40 and return	0.9833	Fleischmann	<i>Loc. cit.</i>
Cream.....	.....	0.8443	Fleischmann	<i>Loc. cit.</i>
Cream.....	.....	0.7	Fjoid	<i>Loc. cit.</i>
Butter.....	.....	0.4	Fjoid	<i>Loc. cit.</i>
Butter.....	31.15	0.5207	Fleischmann	<i>Loc. cit.</i>
Butter.....	.....	0.55	King	Siebel's <i>Compend Mech. Ref. &amp; Eng.</i>

The curves may be divided into three parts as indicated by the vertical lines A, B, C and D. Over the range from C to D we obtain what is, no doubt, the true specific heat of the various materials. From C to B there is a great rise and the specific heat is abnormal—only on apparent specific heat, however. Butter fat is composed of a number of constituents which melt at different temperatures and the abnormal values for specific heats include the latent heats of fusion of the components of the fat. The wide temperature range over which we find a high specific heat is in close agreement with the variations in the results that have been obtained for the melting point of butter fat by various investigators. For many practical purposes the apparent specific heat is of as great value as the true specific heat, provided the value obtained for a particular temperature interval is obtained while applying the heat at such a rate that all of the material meltable in that particular range becomes entirely melted and equilibrium is established. Fleischmann obtained results as high as 1.58 for a 26 per cent cream. These values were probably obtained because of the method employed, which consisted of dropping into the sample a copper cylinder heated to 100° C. All of the readily meltable substances next to the cylinder would be quickly changed to the liquid state, possibly even decomposed to some extent, and, especially if the stirring was not very rapid, an abnormal result would be expected.

The third portion of the curves A to B is particularly interesting because of the marked drop in the specific heat. The values near the freezing point of water are of importance in their bearing on the question of the relation of the specific heats of ice cream mixes to the effect on the palate. An ice cream very rich in fat would not only have a low specific heat at low temperatures, but as is apparent from the very great slopes of the specific heat curves and the high maximum reached, it would absorb heat rapidly with an increase in temperature. From the data obtained

(disregarding other factors) it appears that an ice cream carrying considerable fat, when first coming in contact with the warm palate and tongue would give a sensation that was not disagreeably cold. Then as the temperature increased, because of the absorption of heat by the fusion of the fats, the mass would be automatically maintained cold longer than it otherwise would remain. In short, there is no sensation of extreme coldness but still the mass remains cold for a longer time than if smaller amounts of fat were present.

On the other hand, with low-fat ice creams and sherbets, there is a sensation of extreme coldness when the material is first taken into the mouth, but the mass soon warms up.

As before stated Table V is the summary of the results obtained in this study.

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#### NOTE ON THE PRECIPITATION OF LACTALBUMIN IN COWS' MILK

By W. O. WALKER and A. F. GRANT CADENHEAD

Received April 13, 1914

Having had occasion recently to estimate the albumin in a considerable number of samples of cows' milk, the method at first made use of was that outlined in the "Official and Provisional Methods of Analysis of the Association of Official Agricultural Chemists." According to this method, after removal of the casein by precipitation with acetic acid, and filtering, the filtrate is neutralized with sodium hydroxide, and 0.3 cc. of 10% acetic acid added, and the solution heated to boiling to precipitate the albumin. This method gave unexpectedly low and somewhat varying results. Certain modifications were tried without improvement, notably (a) boiling for a longer time without permitting evaporation, and (b) varying the amounts of acid added after neutralization. The former gave no variation in the amounts precipitated; the latter appeared to work better with 0.5 cc. than with a less quantity of acid, as is here shown:

Sample No.	Per cent albumin using 0.50 cc. acid	Per cent albumin using 0.10 cc. acid
a.....	0.330	0.210
b.....	0.546	0.361

This is rather surprising, as it was supposed that a greater amount of acid would tend to dissolve the precipitated albumin. The average percentage of albumin found when the 0.3 cc. was used, was 0.420, in eight samples of individual cows' milk.



It was found that if the filtrate were allowed to evaporate during continued boiling, successive and decreasing amounts of precipitate might be filtered off. Further, the amount of protein matter in the filtrate from the albumin was correspondingly high, and out of all proportion to the amount of unprecipitated protein that one might expect to find in milk. Consequently it was decided to find a better method of estimating the albumin.

Barthels<sup>1</sup> mentions Sebelien's<sup>2</sup> method of estimating albumin, using Almen's reagent (4 grams nitrogen-free tannic acid + 190 cc. 50 per cent alcohol + 8 cc. 25 per cent acid). This was tried with very satisfactory results. No experimental details being given by Barthels, these were worked out. The best results were obtained by using 10 to 12 cc. of the reagent for a 10 gram sample of milk. The clear filtrate, with washings from the casein—which was precipitated according to the Official Method—was neutralized with sodium hydroxide with the addition of a few drops of phenolphthalein. The pink color was then discharged with one drop of 10 per cent acetic acid, the filtrate, about 200 to 250 cc. in volume, was heated to 40°–45° C., and the reagent added, the mixture stirred continually for two minutes, and then allowed to stand for half an hour before filtering, when the albumin was precipitated in a very fine flocculent form. When filtered immediately after precipitation, some of the precipitate invariably passed through the paper. The precipitate and the paper were then treated according to the Official Kjeldahl-Gunning method, the nitrogen determined, and the result multiplied by 6.34 for albumin.

The protein in the filtrate from the above operation was determined in each case, and was found to show an average of 0.10 per cent.

The following tables show the results obtained by both methods:

TABLE I (PERCENTAGES)

Sample No.	Albumin pptd. by boiling	Protein in filtr.
a.....	0.250	1.22
b.....	0.432	0.54
c.....	0.318	0.80
d.....	0.417	0.70
e.....	0.306	0.40
f.....	0.342	0.55
g.....	0.375	0.47
h.....	0.525	0.49

TABLE II (PERCENTAGES)

Sample No.	Albumin pptd. by Almen's reagent	Protein in filtr.
1.....	0.650	0.120
2.....	0.615	0.105
3.....	0.628	0.102
4.....	0.536	0.044
5.....	0.611	0.129
6.....	0.595	0.075
7.....	0.775	0.165
8.....	0.629	0.061
Average.....		0.100

## SUMMARY

From the above it would appear that the method for estimating albumin as outlined in the Official Bulletin is unreliable.

The above method gives much more satisfactory and uniform results, and is quite as convenient both as regards time and manipulation.

NOTE—The tannic acid used was Merck's "Highest Purity," but it should be tested for nitrogen, and the correction made if protein matter is to be determined in the filtrate from albumin.

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# THE ABSORPTION OF CERTAIN RADICALS BY LEAVES IN VARYING STAGES OF DECAY, AND THE EFFECT OF LEAVES ON THE ABSORPTION OF THESE RADICALS BY A SOIL

By H. A. NOVES

Received April 18, 1914

Soil substances of a humic nature have not been supposed to play the important part in soil absorption. Very little is known of the absorption and adsorption of humus-forming substances as they decay, and their effect on the absorptive capacity of the soil in their different stages of decay. No literature bearing directly on this subject is available. It was for this reason that the following work was undertaken.

The work divides itself into three divisions, the objects of which are to study the absorption of certain radicals by:

I—Freshly fallen leaves and leaf moulds in different stages of decay.

II—Mixtures of soil and leaves.

III—Mixtures of soil and leaves after they had been allowed to remain in contact for a time.

## MATERIALS USED IN THE INVESTIGATION

1—Freshly fallen leaves gathered from the lawn.

2—The freshly fallen leaves after six months decay in the greenhouse.

3—Two leaf moulds. Sample (A) was decayed so that the structure of the leaves was not visible, while in sample (C) the woody portions of the leaves were still discernible.

4—Brown silt loam, unfertilized for years and very poor in organic matter.

5—A mixture of 95 per cent by weight of the brown silt loam, and 5 per cent of the freshly fallen leaves.

6—A mixture, containing 80 per cent of the brown silt loam and 20 per cent of the freshly fallen leaves.

7—Mixtures of the leaves and loam, as above, after six months decay in the greenhouse.<sup>1</sup>

PREPARATION OF THE MATERIALS—All the materials were ground in a hand coffee mill after they were air-dried. All ground well with the exception of the freshly fallen leaves. The ground material passed through a one millimeter sieve. (The woody portions of the leaves were sometimes in pieces five millimeters long.)

The solutions used were approximately tenth normal. The salts used were: potassium bromide, chloride and iodide, calcium hydrogen phosphate, calcium chloride, ammonium chloride, potassium nitrate and magnesium sulfate.

PROCEDURE—Thirty grams of the air-dry material were placed in a 12 oz. salt-mouthed bottle with 200 cc. of the salt containing the radical to be studied. The bottle was closed with a rubber stopper and shaken for fifteen minutes in a shaking machine, and then at intervals by hand. After about 18 hrs. the contents were poured onto a folded filter and the filtrate was returned until the filtrate came through clear. 50 to 80 cc. of the filtrate were collected in a small flask or

<sup>1</sup> The water-holding capacity of the leaves and of the mixtures was determined and they were kept at one-half the results of these determinations while decaying.

<sup>1</sup> Barthel's "Milk and Dairy Products" (Goodwin's Tr.), p. 85.

<sup>2</sup> *Zell. für physiol. Chem.*, 13.

glass stoppered bottle; 10 cc. portions of the filtrate were taken and the determinations carried out by some standard method.

The solutions were always analyzed within a few hours after they were prepared as moulds grew in them if they were allowed to stand. No heat was applied to any of the solutions unless it was called for in the analytical method used.

Water solutions of the materials were made up in the same manner and these with aliquots of the solution containing the radical under investigation constituted the blank and the check determinations.

**ANALYTICAL METHODS**—The chlorides, bromides, and iodides were determined by titrating with silver nitrate, using potassium chromate as an indicator.

The phosphoric acid was determined gravimetrically as magnesium pyrophosphate.

The ammonia was determined by adding strong sodium hydroxide and distilling into standard acid.

The nitrates were determined by the Kjeldahl process modified to include nitrates.

The potassium was determined gravimetrically as potassium chloroplatinate.

Calcium was determined volumetrically, being precipitated as the oxalate, and titrated with potassium permanganate.

The magnesium was determined as the pyrophosphate.

The sulfate was precipitated and weighed as barium sulfate.

**RESULTS**—The results of the blank determinations have been deducted from the figures given in the following tables and for that reason are given here. Water solutions of all the materials studied showed phosphates, sulfates, chlorides, and nitrates to be present in them.

TABLE I—ABSORPTION BY FRESHLY FALLEN LEAVES AND LEAVES IN THREE STAGES OF DECAY  
Calculated per gram of the material used. There was no absorption of Cl, Br, I, NO<sub>3</sub>, Mg nor SO<sub>4</sub>

Radical	PO <sub>4</sub>	NH <sub>4</sub>	K	Ca
Freshly fallen leaves.....	Very slight	0.001835	0.006013	No ab.
Freshly fallen leaves after six mos. decay.....	0.00047	0.002410	0.002740	0.00214
Leaf mould C.....	0.00128	0.002559	0.004078	0.00005
Leaf mould A.....	0.00284	0.003141	0.004175	0.00011

This table shows that

1—The absorption of PO<sub>4</sub> increases as the decay proceeds.

2—The ammonium absorption increases as the decay proceeds.

3—The potassium absorption depends on the state of the material at the time that the test is made.

4—The calcium absorption seems to increase as the decay proceeds.

**SPECIAL EXPERIMENTS**—Freshly fallen leaves and the two leaf moulds were treated with tenth normal benzoic acid in alcohol solution. The leaves showed no absorption of the benzoic acid, while the leaf moulds showed absorption directly proportional to the decay.

Freshly fallen leaves were washed with distilled water. The washed leaves contained less sulfate, chloride, etc., but the washing had no effect on the absorption.

The hygroscopic moisture was determined in the

materials with the result that it was proven that it did not affect the absorption.

Portions of the materials were reground and sieved and the absorption of these sievings was compared to that of the original material with the result that it was determined that the absorption was in some cases slightly affected by the size of the particles.

TABLE II—ABSORPTION BY FRESHLY FALLEN LEAVES, A SOIL, AND TWO MIXTURES OF THE SOIL AND LEAVES  
Calculated per gram of the material used. There was no absorption of Cl, Br, I nor NO<sub>3</sub>

Radical	PO <sub>4</sub>	NH <sub>4</sub>	K	Ca	Mg	SO <sub>4</sub>
Freshly fallen leaves.....	slight	0.001835	0.006013	No ab.	No ab.	No ab.
Brown silt loam.....	0.00273	0.000520	0.002805	0.00021	0.00007	0.00086
95 per cent soil, 5 per cent leaf mixture.....	0.00247	0.001105	0.003305	0.00021	0.00007	0.000658
80 per cent soil, 20 per cent leaf mixture.....	0.00179	0.001137	0.004352	0.00013	0.00006	0.000782
(a) The solution used was hundredth normal.						

This table shows that:

1—The leaves are principally concerned with the absorption of the ammonium and potassium radicals.

2—The absorption of the other materials is due more to the soil than to the leaves.

TABLE III—ABSORPTION BY DECAYING LEAVES, A SOIL, AND TWO MIXTURES OF THE SOIL AND THE DECAYING LEAVES  
Calculated per gram of the material used. There was no absorption of Cl, Br, I nor NO<sub>3</sub>

Radical	PO <sub>4</sub>	NH <sub>4</sub>	K	Ca	Mg	SO <sub>4</sub>
Freshly fallen leaves after 6 mos. decay.....	0.00047	0.00241	0.00274	0.00214	No ab.	No ab.
Brown silt loam.....	0.00273	0.00052	0.00281	0.00021(a)	0.00007	0.00086
95 per cent soil, 5 per cent leaf mix. after 6 mos. decay.....	0.00196	0.00062	0.00230	0.00086	Very slight	No ab.
80 per cent soil, 20 per cent leaf mix. after 6 mos. decay.....	0.00299	0.00148	0.00306	0.00157	Very slight	No ab.
(a) The solution used was hundredth normal.						

This table shows:

1—That the sulfate and the magnesium which the soil would absorb are being supplied by the leaves.

2—Irrregularity, probably due to the different stages of decay of materials since:

(a)—The capillarity of the mixtures was observed to be very different.

(b)—Bacterial decomposition was not the same because of differences in the pore space, the temperature and the materials used.

3—That the absorption of the soil is increased by having decaying humus-forming material in it.

#### CONCLUSIONS

1—Leaves, undecayed and in different stages of decay show absorption for certain radicals. This absorption (for the radicals studied) does not always increase with the decay.

2—The color of the solutions obtained by treating the same material with a different salt may not be the same. This indicates that some of the absorption may be chemical combination.

3—When soil is added to the leaves they still absorb.

4—The mixtures of the soil and the leaves both before and after decay has started do not absorb on the same basis that their constituents do.

5—SUMMARY—Humus-forming substances such as leaves do play a part in soil absorption and the part that they play depends on their state of decay.

ADDENDUM—As stated above no literature bearing directly on this subject was found by the author. The following literature will be of interest to anyone wishing to undertake work of this kind.

*Compt. rend.*, **132** (1901), 435-437.

*Ibid.*, **141** (1905), 433-445.

An abstract in *Exp. Sta. Re.*, **13**, 534

*Landwirtschaftliche Jahrbücher*, **41**, 717-754.

This work was undertaken at the suggestion of Dr. Ernest Anderson of the Massachusetts Agricultural College and was completed in the Department of General and Agricultural Chemistry of that college.

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## DISTRIBUTION OF CERTAIN CONSTITUENTS IN THE SEPARATES OF LOAM SOILS

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Received April 6, 1914

### INTRODUCTION

The determinations given in this paper were made with a view to finding the distribution of the commoner elements in the finer separates of a series of loam soils. The analyses were made by fusion methods, so that the entire amount of the constituent was determined in each case. In many former experiments in this direction only the material extracted by digesting with acid of certain concentration was determined. Previous related work along this line was reviewed by Failyer, Smith and Wade, in *Bulletin No. 54*, Bureau of Soils, U. S. Department of Agriculture. Little work has been done along this line since this publication was issued. The bulletin of Failyer, Smith and Wade gives the determinations of total lime, magnesia, potash and phosphoric acid. The present work covers in addition the distribution of silica, iron oxide, alumina, titanium oxide, zirconia and soda.

Twenty-seven soils of various types were examined by Failyer, Smith and Wade for the distribution of phosphoric acid, potash, lime, and magnesia among the separates. Among other conclusions, they found that these constituents were more concentrated in the finer particles and the segregation is more marked in soils that have been subject to extreme weathering.

### DESCRIPTION OF SAMPLES

Ten soils in all were examined. They were as follows:

1—Volusia silt loam, soil, 0-8 inches, 3 1/2 miles S. W. Naples, N. Y. Glacial origin. Formed mainly from sandstone and shale material, with some brought in by glacial action.

2—Cecil sandy loam, soil, 0-8 inches, 3 1/2 miles S. W. Charlotte, N. C. Derived mainly from granite, gneiss and to a smaller extent from other crystalline rocks. A Piedmont Plateau type.

3—Durham sandy loam, soil, 0-10 inches, 1 1/4 miles N. E. Archer, N. C. Formed mainly of materials derived from light-colored, medium-grained granite. A Piedmont Plateau type, occurring in the region bordering the Coastal Plain. Contains a relatively large percentage of potash feldspar, derived from the parent rock.

4—Hagerstown loam, soil 0-8 inches, 1 mile N. W. Conshohocken, Pa. One of a group of soils resulting from the weathering of limestone. Sands rich in mineral species.

5—Norfolk sandy loam, soil, 0-14 inches, 3 1/2 miles S. W. Laurinsburg, N. C. An important type in the Coastal Plain Province. Derived from unconsolidated marine deposits.

6—York silt loam, soil, 0-10 inches, Bethany, S. C. Formed of materials derived from imperfectly crystalline rocks, mainly talcose and micaceous schists. Piedmont Plateau Province.

7—Louisa loam, soil, 0-12 inches, Trevelians, Va. Derived mainly from talcose and micaceous schists and imperfectly crystalline slates. Piedmont Plateau Province.

8—Penn silt loam, soil, 0-9 inches, 1 1/2 mile W. Penn Square, Pa. Formed mainly from sandstones of triassic age. Piedmont Plateau Province.

9—Gloucester stony loam, 3 miles E. of Marlboro, N. H., soil, 0-8 inches. A glacial soil derived mainly from granite and mica schist, but with some admixture of other materials brought by glacial action.

10—Carrington loam, 0-11 inches, Lawville, Wis. Derived through weathering, from glacial till. Glacial and Loessial Province.

### PREPARATION OF SEPARATES

The separates of the soils were obtained by sedimentation and centrifuging as described in *Bulletin 84*, Bureau of Soils, Department of Agriculture, 1912.<sup>1</sup>

The diameters of the particles making up the separates used were as follows:

Diameter in millimeters	Separates
0.1-0.05	Fine sand
0.05-0.025	Coarse silt
0.025-0	Fine silt and clay

After the samples were ground and had reached equilibrium with the moisture of the air, they were ready for analysis. Moisture lost at 110° C. was determined and calculations made on the basis of samples dried at this temperature.

### METHOD OF ANALYSES

The determinations were made by fusion methods following very closely those given in *Bulletin 422* of the U. S. Geological Survey, "The Analysis of Silicate and Carbonate Rocks."

Silica, iron oxide, titanium oxide, lime, and magnesia were determined first by fusing a three-quarter gram sample.

A 2 gram sample was used for the determination of zirconia. Zirconia was, after separation from larger amounts of silica, alumina, etc., taken up in dilute sulfuric acid solution and precipitated as phosphate, fused, and again brought into solution and precipitated. The weight of the dioxide is calculated from the amount of the phosphate.

For the determination of phosphoric acid the sample was fused with sodium carbonate. After removing silica the phosphorus is precipitated as yellow phosphomolybdate of ammonium, dissolved in ammonia and later precipitated as magnesium ammonium phosphate and weighed as magnesium pyrophosphate. The alkalies were determined by the J. Lawrence Smith method. Alumina was determined by subtracting from the iron group the sum of the other oxides present.

The following tables give the results of the analyses.

### DISTRIBUTION OF THE ELEMENTS IN GENERAL

The order of abundance of silica, alumina and iron oxide in these separates is that usually found in soils. In every separate examined the percentage of silica (SiO<sub>2</sub>) is greater than that of any other oxide. In all cases, except two, alumina is second in order of abundance. In most cases iron is third.

As with soils hitherto examined, the percentage of silica decreases from the coarser to the finer particles. Zirconia follows the same variation except in two cases.

Iron oxide, alumina, titanium (with two exceptions), potash (with three exceptions), and phosphoric acid

<sup>1</sup>The mechanical analyses were made by Messrs. L. A. Kolbe and W. B. Page of the Bureau of Soils



TABLE I—PERCENTAGE COMPOSITION OF SOIL SEPARATES

CONSTITUENT	No. 1 VOLUISA SILT LOAM			No. 2 CERIL SANDY LOAM			No. 3 DURHAM SANDY LOAM			No. 4 HAGERSTOWN LOAM			No. 5 NORFOLK SANDY LOAM		
	Fine sands	Coarse silt	Fine silt and clay	Fine sands	Coarse silt	Fine silt and clay	Fine sands	Coarse silt	Fine silt and clay	Fine sands	Coarse silt	Fine silt and clay	Fine sands	Coarse silt	Fine silt and clay
SiO <sub>2</sub> .....	90.05	87.78	46.09	94.79	86.89	45.92	79.44	80.53	55.29	76.23	82.26	42.96	98.99	98.17	58.71
Fe <sub>2</sub> O <sub>3</sub> (a).....	1.89	1.69	10.51	1.21	1.31	6.46	1.27	1.05	4.84	2.32	1.67	11.13	0.35	0.52	1.97
Al <sub>2</sub> O <sub>3</sub> .....	5.08	5.66	22.52	2.73	6.86	28.14	11.39	10.08	24.80	8.01	8.19	23.80	0.40	1.48	18.44
TiO <sub>2</sub> .....	0.64	0.95	0.98	0.87	1.05	1.19	0.79	1.11	1.86	1.03	1.16	1.01	0.57	1.12	3.38
CaO.....	0.56	0.47	0.70	0.33	0.13	0.26	0.88	0.68	0.43	1.72	0.97	1.27	0.05	0.24	0.28
MgO.....	Trace	0.15	1.03	Trace	Trace	0.36	Trace	Trace	Trace	2.06	0.84	1.44	0.01	0.03	Trace
ZrO <sub>2</sub> .....	0.14	0.07	0.01	0.11	0.06	0.01	0.14	0.20	0.03	0.11	0.11	0.01	0.06	0.18	0.07
Na <sub>2</sub> O.....	0.79	1.06	0.40	0.13	0.06	0.20	1.58	1.31	0.24	0.27	0.83	0.37	Trace	0.08	0.26
K <sub>2</sub> O.....	0.99	1.06	1.66	0.79	1.66	1.99	5.56	4.35	1.62	3.83	2.54	2.02	Trace	0.15	0.63
P <sub>2</sub> O <sub>5</sub> .....	0.16	0.08	0.44	0.10	0.12	0.23	0.12	0.14	0.17	0.20	0.03	0.48	0.08	0.03	0.08

CONSTITUENT	No. 6 YORK SILT LOAM			No. 7 LOUISIA LOAM			No. 8 PENN SILT LOAM			No. 9 GLOUCESTER STONY LOAM			No. 10 CARRINGTON LOAM		
	Fine sands	Coarse silt	Fine silt and clay	Fine sands	Coarse silt	Fine silt and clay	Fine sands	Coarse silt	Fine silt and clay	Fine sands	Coarse silt	Fine silt and clay	Fine sands	Coarse silt	Fine silt and clay
SiO <sub>2</sub> .....	97.51	75.03	38.97	97.35	89.11	57.07	85.16	84.27	46.05	77.19	64.13	22.55	88.33	85.04	41.62
Fe <sub>2</sub> O <sub>3</sub> .....	0.82	2.37	7.13	1.24	2.79	7.11	2.46	1.81	10.09	2.95	4.80	17.02	2.07	1.80	9.02
Al <sub>2</sub> O <sub>3</sub> .....	1.07	1.08	31.33	0.92	3.72	18.51	7.52	8.11	23.23	12.56	18.38	16.76	5.15	6.91	18.14
TiO <sub>2</sub> .....	0.41	0.33	0.45	0.55	0.44	1.70	0.70	1.14	1.04	1.20	1.15	1.09	0.45	0.69	0.68
CaO.....	0.11	0.19	0.36	0.27	0.34	0.22	0.31	0.35	0.98	1.09	0.78	0.73	0.59	0.67	1.20
MgO.....	Trace	0.04	Trace	0.06	0.15	0.26	0.35	0.40	1.05	0.62	1.05	0.30	0.28	0.37	1.21
ZrO <sub>2</sub> .....	0.02	0.03	0.05	0.11	0.15	0.04	0.08	0.11	0.01	0.09	0.08	0.01	0.07	0.07	0.01
Na <sub>2</sub> O.....	0.06	0.59	0.61	Trace	0.24	0.14	2.18	1.78	0.41	1.70	1.52	0.49	0.56	1.12	0.36
K <sub>2</sub> O.....	0.22	3.72	5.40	0.03	0.76	1.85	0.58	1.38	2.87	1.40	2.60	1.79	2.40	2.22	1.67
P <sub>2</sub> O <sub>5</sub> .....	0.04	0.09	0.12	0.10	0.01	0.24	0.06	0.02	0.29	0.15	0.13	0.43	0.10	0.04	0.46

(a) Includes both ferric and ferrous iron.

(with one exception) increase in percentage composition with the fineness of the particles.

Lime, magnesia and soda seem to follow no general rule. The higher content of potash in the coarser separates of three soils is due to the presence of coarse crystals of potash feldspar. As a rule potash is segregated in the finer particles.

TABLE II—AVERAGE, MAXIMUM AND MINIMUM AMOUNTS OF THE SEVERAL MINERAL CONSTITUENTS FOUND IN THE DIFFERENT SEPARATES

PERCENTAGES									
		Fine silt and clay					Fine silt and clay		
Constituent		Fine sands	Coarse sands		Constituent		Fine sands	Coarse sands	
SiO <sub>2</sub>	Av.	88.50	83.05	45.52	MgO	Av.	0.40	0.33	0.54
	Max.	98.99	95.37	58.71		Max.	2.06	1.05	1.56
	Min.	76.23	64.13	22.55		Min.	Trace	Trace	Trace
Fe <sub>2</sub> O <sub>3</sub>	Av.	1.66	1.96	8.73	ZrO <sub>2</sub>	Av.	0.09	0.11	0.02
	Max.	2.95	4.80	17.02		Max.	0.14	0.20	0.07
	Min.	0.35	0.52	3.97		Min.	0.02	0.03	0.01
Al <sub>2</sub> O <sub>3</sub>	Av.	5.48	8.44	22.57	Na <sub>2</sub> O	Av.	0.73	0.86	0.35
	Max.	12.56	18.28	31.33		Max.	2.18	1.78	0.61
	Min.	0.40	1.48	16.76		Min.	Trace	0.06	0.14
TiO <sub>2</sub>	Av.	0.72	1.11	1.34	K <sub>2</sub> O	Av.	1.58	2.04	2.15
	Max.	1.20	2.44	3.38		Max.	5.50	4.35	5.40
	Min.	0.41	0.33	0.45		Min.	Trace	0.76	0.63
CaO	Av.	0.59	0.48	0.44	P <sub>2</sub> O <sub>5</sub>	Av.	0.11	0.08	0.29
	Max.	1.72	0.97	1.27		Max.	0.20	0.14	0.36
	Min.	0.05	0.13	0.22		Min.	0.04	0.01	0.08

Table II of averages and maximum and minimum results shows the general composition of the finer separates of loams and direction of segregation of constituents in them.

BUREAU OF SOILS  
U. S. DEPARTMENT OF AGRICULTURE  
WASHINGTON

### THE PREPARATION OF "NEUTRAL" AMMONIUM CITRATE<sup>1</sup>

By ERMON D. EASTMAN AND JOEL H. HILDEBRAND

In the official method for the determination of phosphoric acid in fertilizer, it is necessary to use a "neutral solution" of ammonium citrate of density 1.09 at 20°. A number of methods have been proposed for preparing this solution, such as those using various indicators,<sup>2</sup> the titration by conductivity,<sup>3</sup> the extraction and heat of reaction methods,<sup>4</sup> and an analytical method proposed by Patten and Marti.<sup>5</sup> Mention

should also be made of the recent paper by Rudnick and Latshaw.<sup>1</sup> The result has been that while one analyst can usually reproduce his own results, the results of different analysts have frequently shown wide variations. Thus McCandless,<sup>2</sup> while referee on phosphoric acid for the Association of Official Agricultural Chemists, found solutions made by different men to vary in their ratio of ammonia to citric acid from 1:3.775 to 1:4.180. The commercial importance of this solution requires that it should be defined accurately and that the method for its preparation should be simple and reliable. Reference to this problem by one of us in an address<sup>3</sup> at the Milwaukee meeting of the American Chemical Society led to a request from the Fertilizer Division for cooperation in its solution, resulting in the work which is described in the following pages.

#### DEFINITION OF A "NEUTRAL SOLUTION"

In defining the solution it is necessary to bear in mind the fact that salts of weak acids and bases do not necessarily react neutral in aqueous solution. A salt-like sodium acetate will react alkaline, due to hydrolysis, while one like ammonium chloride will react acid. When both a weak acid and a weak base are involved as with ammonium acetate, considerable hydrolysis will take place, and the solution will contain an appreciable quantity of free acid and base, though the extent to which the solution would depart from neutrality would depend on the relative strength of the acid and base. A solution of ammonium citrate, therefore, shows considerable hydrolysis, and contains free acid and free base, even when the citric acid and the ammonia are present in equivalent quantities. For this reason it is folly to expect to prepare a neutral solution of ammonium citrate by one of the methods that has been proposed, *i. e.*, to add an excess of ammonia and let stand till the excess has volatilized. Any solution of ammonium citrate, whether acid or alkaline, contains free ammonia, which would be gradually removed on standing open to the air and more rapidly by boiling.

<sup>1</sup> Presented at the 49th Meeting of the A. C. S., Cincinnati, April 4-6, 1914.

<sup>2</sup> Bull. Bur. Chem., **107**, 1; **133**, 11.

<sup>3</sup> Hall and Bell, *J. Am. Chem. Soc.*, **4** (1912), 443.

<sup>4</sup> Bell and Cowell, *J. Am. Chem. Soc.*, **35** (1913), 49.

<sup>5</sup> This Journal, **6** (1913), 567.

<sup>1</sup> This Journal, **5** (1913), 998.

<sup>2</sup> Bull. Bur. Chem., **122**, 147.

<sup>3</sup> Hildebrand, *J. Am. Chem. Soc.*, **35** (1913), 848, 1538.

Whether or not a solution containing equivalent amounts of ammonia and citric acid, which we shall call the normal salt, will be neutral, acid, or alkaline, depends upon the relative affinity of ammonium ion and citrate ion for hydroxyl and hydrogen ion, respectively, of water; in other words, upon the relative ionization of  $\text{NH}_4\text{OH}$  and  $\text{HC}_6\text{H}_5\text{O}_7^-$ . Since the dissociation constants of the three hydrogen ions of the citric acid molecule are not known separately, the question of the neutrality of the solution must be determined experimentally. This is very conveniently done by means of the hydrogen electrode, as previously described by one of us.<sup>1</sup> The results of such titration in the neighborhood of the neutral point are shown in Fig. 1. It was pointed out in the previous paper

the former results from the analytical and conductivity methods rather than the latter, it will doubtless be less disturbing to present practice to recommend it rather than the truly neutral solution. If desired, the procedure we here recommend could easily undergo the slight modification necessary to yield the neutral solution.

We therefore define the solution as one containing equivalent quantities of citric acid and ammonia, and add that a hydrogen electrode immersed in it will show an E. M. F. against a normal calomel electrode of 0.71 volt, from which the hydrogen ion concentration is calculated to be  $10^{-7.4}$ .

#### PRINCIPLES OF PROPOSED METHOD

The quickest and most reliable way to make up a solution of ammonium citrate of equivalent acid and base content would be to use the hydrogen electrode in the form such as was described by one of us.<sup>1</sup> The whole curve would not need to be obtained. It would suffice to set the opposing E. M. F. at 0.71 volt and add ammonia until the galvanometer or electrometer just deflected in the opposite direction on pressing the key. This would require the apparatus described for such purposes, which would entail some expense, although it would prove a useful addition to an analytical laboratory. Since this is too much to expect, however, we have devised a method whereby the same result may be achieved by the use of an indicator with a slightly greater expenditure of time and labor.

The comparatively slight change in hydrogen ion concentration between a solution containing an excess of acid and one containing an excess of ammonia, showing itself in the not very rapid rise in the curve, makes clear the reason for the unsatisfactory behavior of indicators in this titration. Most indicators require a change in hydrogen ion concentration of nearly a power of ten in order that their colors may be entirely changed. Within that range some color standard is necessary for comparable results and this makes the results very subjective, as ordinarily worked. (By reference to Fig. IV of the paper on the hydrogen electrode, to which frequent reference has been made, it will be at once evident that the hydrogen ion concentration of sodium citrate changes far more rapidly through the neutral point than that of ammonium citrate, so that the former gives a sharp end point with an indicator while the latter does not.)

In order to fix the hydrogen ion concentration of the solution accurately it is necessary to choose an indicator whose color change is a maximum at the desired point, and then to fix the desired color by means of a standard solution which will give to the indicator the same color that it would get in a solution of the normal ammonium citrate of the prescribed density. It was found that a standard solution of the same hydrogen ion concentration as the citrate solution would not give the same color with the indicators tried. This is to be attributed to the large salt effect of such a concentrated solution. The acidity of the comparison solution had therefore to be adjusted by trial.

For the comparison solution we used a mixture of

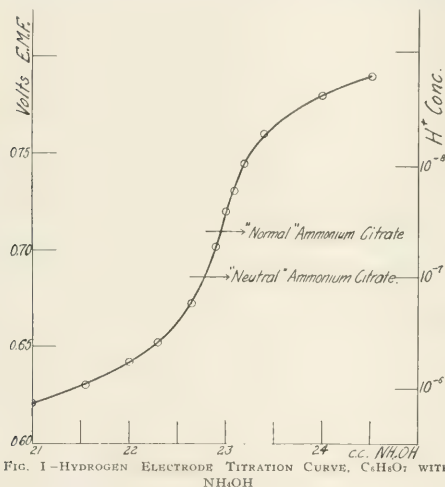


FIG. 1—HYDROGEN ELECTRODE TITRATION CURVE,  $\text{C}_6\text{H}_8\text{O}_7$  WITH  $\text{NH}_4\text{OH}$

that the point of inflection of such a curve represents the normal salt, while E. M. F. of 0.69 volt against a normal calomel electrode, corresponding to a hydrogen ion concentration of  $10^{-7}$  at room temperature indicates a truly neutral solution. (In this calculation the liquid contact potential has been neglected, as where two nearly neutral solutions of high concentration are in contact the potential can be disregarded where an accuracy of a centivolt is sufficient, as is the case here.) It will be seen that the solution of the normal salt is slightly alkaline, having a hydrogen ion concentration of  $10^{-7.4}$ . It, therefore, becomes a question which solution should be selected. It may be noted that the acidity varies most rapidly with the composition along this portion of the curve, and that solutions containing a definite excess of citric acid or ammonia would not need to be made nearly as carefully in order to have a uniform hydrogen ion concentration, and, presumably therefore, a uniform action on phosphoric acid bearing material. Since, however, the neutral solution is prescribed legally, as the official method, we will show how it can be made, and since the normal and neutral solutions are so nearly alike, and since

<sup>1</sup> Loc. cit.

<sup>1</sup> Loc. cit.

mono- and disodium phosphates. The change from a solution containing the ions  $\text{PO}_4^{3-}$  and  $\text{HPO}_4^{2-}$  to one containing  $\text{HPO}_4^{2-}$  and  $\text{H}_2\text{PO}_4^-$  is marked by a sudden increase in hydrogen ion concentration which is shown very satisfactorily by phenolphthalein. The change from the latter pair of ions to the mixture  $\text{H}_2\text{PO}_4^-$  and  $\text{H}_3\text{PO}_4$  causes another sudden increase

it only. Changes would have to be made in the standard of comparison if any other indicator were employed.

#### PROCEDURE RECOMMENDED

For the preparation of citrate solution in two-liter lots, dissolve 370 grams in 1500 cc. of water, and nearly neutralize with concentrated ammonia solution. Cool to  $20^\circ$  and then add more ammonia from a buret until a 10 cc. portion of the thoroughly stirred solution, with a suitable quantity of rosolic acid, shows the same color in a Nessler tube that the same amount of indicator gives with a 10 cc. portion of a phosphate solution prepared as follows:

Titrate a 25 cc. portion of an approximately 0.1 molar stock solution of  $\text{Na}_2\text{HPO}_4$  (to which dilute  $\text{HCl}$  or  $\text{NaOH}$  has been added until phenolphthalein is just colorless in the solution) with  $N/10$   $\text{HCl}$  and methyl orange. To a fresh 25 cc. portion (neutral to phenolphthalein) add  $1/6$  of the volume of  $\text{HCl}$  used in the previous titration. Stir well and use a suitable portion for the color standard above. When the citrate is neutralized, bring the solution to a specific gravity of 1.09 at  $20^\circ\text{C}$ . When small quantities are to be made it is simpler to prepare a volume of phosphate equal to the desired volume of citrate, thus avoiding the withdrawal of samples. For the 10 cc. portions two drops (100 drops = 3 cc.) of rosolic acid, 0.25 gram dissolved in 50 cc. alcohol and 50 cc. water, gave a good color.

The method is sensitive to about 0.1 per cent of the total  $\text{NH}_4\text{OH}$  involved. Three distinct samples of "neutral" citrate prepared by the above formula, and subsequently tested with the hydrogen electrode showed  $(\text{H}^+)$  concentration of  $10^{-7.41}$ ,  $10^{-7.92}$ , and

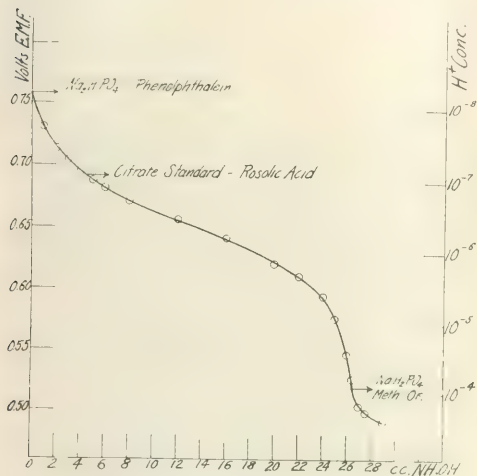


FIG. II—TITRATION OF  $\text{Na}_2\text{HPO}_4$  WITH  $\text{HCl}$

of acidity indicated very sharply by methyl-orange. Between these points the change in acidity is very slow, so that small differences in the concentrations make but little change in the acidity, as shown by the curve in Fig. II. The difference in the end points with these two indicators, on titrating a solution of disodiumhydrogenphosphate, serves to fix the concentration of phosphate in the solution, and it is then easy to transform a part of this by addition of the proper amount of hydrochloric acid, so that a solution of definite hydrogen ion concentration is obtained, subject to a minimum of variation on account of impurities or errors in the manipulation.

In choosing an indicator, alizarin, guaiacum tincture, neutral red, cryanin, hematein, rosolic acid and azolitmus were compared. Considerations such as the sharpness of the change at the desired point, the nature and permanence of the colors, and the adaptability to the standard solution adopted, led to the final selection of rosolic acid. The figures given apply to

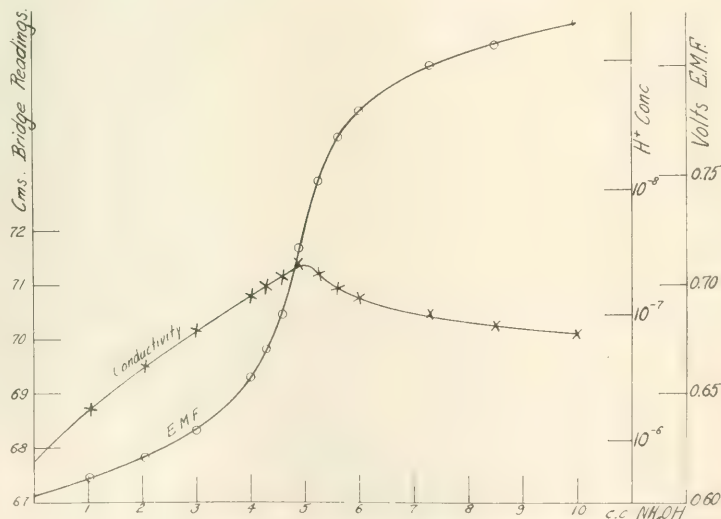


FIG. III—CONDUCTIVITY AND E.M.F. CURVES, TITRATION OF CITRIC ACID WITH AMMONIA

$10^{-7.50}$ , respectively, the largest error being 0.1 per cent. The electrode method was finally compared with the



conductivity method by a titration in which bridge readings were made simultaneously with E. M. F. readings. The results appear in the curves of Fig. III, which show satisfactory agreement in the abscissae.

#### SUMMARY

With the aid of the hydrogen electrode an indicator method for the preparation of tri-ammonium citrate has been developed. The  $H^+$  concentration given by solutions of this salt of 1.09 specific gravity is shown to be  $10^{-7.4}$ . This concentration is obtained in the preparation of the citrate by the use of an easily prepared color standard, made by mixing HCl and  $Na_2HPO_4$  solution. The results of a simultaneous determination of the "neutral point" with the electrode and conductivity methods are shown graphically, and there are given results of several trials of the formula suggested.

NOTE—It seems very likely that the difficulties of the fertilizer chemist in determining available phosphate are not due entirely to lack of uniformity in the ammonium citrate solution used. It may be impossible to distinguish sharply between "reverted" and "available" phosphate by means of neutral ammonium citrate solution. For example, it might be found that available phosphate is barely dissolved by a citrate solution having a hydrogen ion concentration of  $10^{-8}$ , while reverted phosphate is not greatly affected until a hydrogen ion concentration of  $10^{-4}$  is reached. Obviously the best solution for extraction would, in that case, be one whose hydrogen ion concentration is  $10^{-6}$ , and remains so during the extraction. A solution whose hydrogen ion concentration varied between  $10^{-7}$  and  $10^{-8}$  would dissolve uncertain amounts of available phosphate. Furthermore, as mentioned in the above paper, solutions of the normal ammonium citrate have a hydrogen ion concentration most subject to variation, while solutions containing an excess of acid or base would be changed much less by an alteration in the amount of that excess. By reference to the paper by Hildebrand<sup>1</sup> it will be seen (Fig. IV) that the same considerations apply to the proposal to use sodium citrate. The hydrogen ion concentration of an acid solution would be far less affected than would that of one nearly neutral by small variations in the amount of acid present. If an acid solution will not sharply differentiate available and unavailable phosphate, then recourse must doubtless be had to the ammonium salt with an excess of ammonia.

It may also be found desirable to maintain a definite hydrogen concentration during the digestion by means of a suitable indicator, adding ammonia or citric acid as needed to maintain a definite color.

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#### A PROCEDURE FOR SEPARATING ORGANIC AMMONIATES FROM THE MINERAL PORTION OF COMMERCIAL FERTILIZERS<sup>2</sup>

By C. H. JONES and G. F. ANDERSON

The separation and identification of animal and

Low 111

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vegetable ammoniates in commercial fertilizers is a subject of considerable interest and importance to chemists who have charge of analytical work in connection with the enforcement of state fertilizer laws.

The alkaline and neutral permanganate methods for organic nitrogen activity are now quite generally employed in many control laboratories. When properly interpreted they are capable of making reliable differentiations between high and low grade organic ammoniates as regards their activity or availability as nitrogenous plant food.

For several years past the writers have taken an active interest in these problems both as regards laboratory methods and their control by pot experiments. In connection with these lines of investigation we have endeavored to secure some satisfactory method for separating quickly the organic nitrogenous portion of commercial fertilizers from the mineral nitrogen, acid phosphate and potash salts. Several procedures have been tried but with indifferent success.

The scheme about to be described was perfected last year and employed as extensively as time permitted on many commercial fertilizer and crude nitrogenous stock samples.

#### METHOD

Prepare the sample by drying from 100 to 600 grams of the material, preferably unground, at a temperature of not over 170° F. Cool and weigh. The amount taken depends on the nature of the material and on the quantity of the organic portion desired. Nearly fill a suitable beaker with carbon tetrachloride and add the sample in 25 to 50 gram portions. Stir and allow to settle. Skim off the portion that floats and throw on to a dry filter. A tin tablespoon is very serviceable for this purpose. Continue this procedure until the entire sample has been thus treated, using more carbon tetrachloride and another beaker if necessary. Dry the filter containing the organic portion in an air bath. Cool, weigh and preserve for microscopical and chemical analysis.

The bulky residue that sinks is transferred to a 2 liter flask, the filtrate from the organic portion is added, and the carbon tetrachloride recovered by distillation in a covered water bath. The residue remaining in the flask can be removed easily after final drying in an air or vacuum bath and is then cooled, weighed and analyzed if desired.

It has been found advisable in many cases to screen the sample previous to treatment, through a 1 mm. sieve and make the carbon tetrachloride separation on the two portions separately. If the odor of the reagent proves offensive a small exhaust fan placed on the desk near the beaker with outlet pipe extending outside is recommended, or the separation may be made under a hood.

The following summary shows the behavior of many of the materials used in fertilizer manufacture.

FLOATS ON CARBON TETRACHLORIDE—Dried blood, fish, tankage, hoof meal, horn meal, leather, kanona (tankage, morocco clippings), acotin, cottonseed meal, castor meal, castor pomace, beet refuse compound, nitrogenous manure, casein, peat, garbage (tankage, tartar pomace, mowrah meal, rape meal, soda bean meal, wheat gluten, tobacco stems, fillerine (partly), cinders (certain types)).

**SINKS IN CARBON TETRACHLORIDE** Ground bone, nitrate of lime, cyanamid, grape pomace, aluminum nitride, nitrate of soda, sulfate of ammonia, acid phosphate, rock phosphate, basic slag, dissolved bone black, animal charcoal, muriate and sulfate of potash, kaimit

Table I shows the separation as regards the organic portions of 14 commercial fertilizers and 2 tankages. They have been selected from some 35 samples as being representative of the extremes and averages thus far found.

An inspection of the table shows large variations in the nitrogen content of the mixtures that contribute to furnish the organic nitrogen found in commercial fertilizers. It varies from 2.54 per cent in No. 12 to 11.65 and 12 per cent in Nos. 9 and 13. The water-insoluble nitrogen indicates similar ranges. The inorganic portions from the samples above enumerated have been tested as to their insoluble nitrogen content and its activity determined. The activity found compares favorably with that shown in Table I in all but two cases. In other words a high activity

No claim is made that the separation is absolute. The scheme, however, serves to separate readily the major portion of the organic nitrogen present, in amounts sufficiently large to enable one to conduct microscopical and chemical analyses and pot experiments.

Numerous other applications suggest themselves, among them being the separation of sand, dirt and mineral salts from organic drugs, feeding stuffs and condimental feeds.

#### CLASSIFICATION FOR ORGANIC NITROGEN ACTIVITY AS DETERMINED BY THE ALKALINE PERMANGANATE METHOD

PER CENT ACTIVITY	PERCENTAGE OF NITROGEN ACTIVITY
70-80	* Dried blood
60-69	* Castor
50-59	* Fish meal
40-49	* H. G. tankage
	* Hoof meal
	* Soluble portion of a properly made base mix
	* Kanona tankage
	* Medium tankage
	* Bone meal
	* Cottonseed meal
	* Tankage
	* Castor pomace
	* Tartar pomace
	* Leather preparations
	* Peat
	* Garbage tankage
	* Mowrah meal
	* Grape pomace
	* Beet refuse compound
	* Insoluble portion of a properly made base mix
	* Tobacco stems
	* Fillerine

The above classification of materials used in the manufacture of commercial fertilizers may prove of interest in this connection.

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#### THE AVAILABILITY OF NITROGEN IN KELP

By JOHN A. CLEEN  
Received April 14, 1914

In view of the widespread interest in kelp as a possible source of American potash, some information as to the value and nature of the nitrogen present becomes a factor of considerable importance. The average of a large number of analyses made by Mr. T. C. Trescott,<sup>1</sup> of the Bureau of Chemistry, shows an average of approximately 2 per cent of nitrogen. If it is proposed to market dry kelp the value of this amount of nitrogen present is apparent.

In the experiments by the author different methods were followed in order to determine the availability of the nitrogen. Briefly they consisted in following the official alkaline permanganate method,<sup>2</sup> and later with modifications of the same. An attempt was also made to secure availability percentages by using the neutral permanganate method but this was found impractical because of a bulky residue and its resistance to filtration. Table I gives the results obtained in the various experiments.

It will be noticed that by using the official method which provides for an amount of the sample equivalent to 50 mg. of total nitrogen, the availability percentages range from 13.44 per cent in sample number 40 to 44.80 per cent in sample number 19. By pursuing the column farther it will be observed that the per cent of availability generally increases with a decrease in the amount of sample used. In other words it appears that the per cent of availability is inversely proportional to the amount of sample.

Kelp contains on the average about 60 per cent organic matter. Assuming the average nitrogen content to be about 2 per cent, the amount of sample

<sup>1</sup> THIS JOURNAL, 4, 431; 5, 287 and 729; 6, 19.

<sup>2</sup> Report on nitrogen *Bull.* 162, Bur. of Chem.

TABLE I ORGANIC PORTION FLOATS ON CARBON TETRACHLORIDE

Fertilizer	Per cent nitrogen		Water-insoluble nitrogen by alkaline permanganate method	Per cent	REMARKS
	Grams obtained	Total	Water-soluble		
1.....	45	7.86	2.07	5.79	69
2.....	44	9.48	3.03	6.45	75
3.....	49	6.80	1.40	5.40	66
4.....	34	9.16	3.02	6.14	68
5.....	82	9.48	2.18	7.30	75
6.....	26	4.28	0.84	3.44	45
7.....	92	4.77	1.47	3.30	61
8.....	55	5.93	1.97	3.96	65
9.....	80	11.65	1.26	10.39	78
10.....	11	5.12	1.12	4.00	45
11.....	28	4.70	1.47	3.23	41
12.....	78	2.54	0.79	1.75	45
13.....	7	12.00	0.00	12.00	74
14.....	46	4.50	1.62	2.91	44
Tankage.....	79	7.58	0.65	6.93	73
15.....	99	10.24	0.57	9.67	76

in the separated organic portion as determined by laboratory methods was nearly always accompanied by a similar activity for the water-insoluble nitrogen carried down with the mineral portion of the sample.

It should be noted that ground bone sinks in the reagent employed. The sunk portion, therefore, in the two tankages was largely bone. This was indicated not only by visual inspection but by its nitrogen content of 2.32 and 2.17 per cent, respectively, as well as by the  $P_2O_5$  present.

A relatively high water-insoluble nitrogen percentage in the mineral portion of a fertilizer that sinks by this procedure is indicative of bone especially if the activity by the alkaline permanganate method is over 60 per cent.

Certain materials other than those listed under the column headed "Remarks" have been noted in many of the samples examined. Their nature will be further studied when time permits. One in particular is worthy of mention. It occurs as small black pellets, which crumble easily between the fingers. Analysis shows these pellets to contain 3.12 per cent total nitrogen and 1.60 per cent water-insoluble nitrogen with an activity measured by the alkaline permanganate method of 51 per cent.

		TABLE I					
No.	Serial No.	Description	Per cent of total N available				
			A	B	C	D	E
<i>Nereocystis luetkeana</i>							
4	R. 4	Fronds	2.57	35.28	63.84	83.50	88.25
5	R. 5	Fronds	2.71	39.76	69.44	82.68	89.60
6	R. 6	Fronds	2.53	36.40	62.72	92.96	96.28
8	R. 8	Stipes	2.21	28.00	43.68	68.19	83.08
9	R. 9	Stipes	1.46	35.84	58.24	75.92	86.30
<i>Macrocystis pyrifera</i>							
11	R. 11	Stipes and Pneumatocysts	1.37	22.40	34.72	95.18	98.10
12	C. 1		2.15	34.16	53.76	84.65	98.14
13	C. 2		2.72	39.40	59.36	76.47	99.71
19	C. 7		3.17	44.80	72.80	85.49	99.94
20	C. 8		2.11	30.24	45.92	84.35	91.94
21	C. 9		2.16	31.36	48.16	89.81	99.63
22	C. 10		2.38	26.88	47.04	67.65	99.97
<i>Nereocystis luetkeana</i>							
23	C. 11		2.22	31.36	56.00	72.97	91.00
<i>Macrocystis pyrifera</i>							
26	C. 14	Young plant	2.18	35.28	56.00	81.65	100.07
27	C. 15	Old plant	1.00	31.92	49.28	84.35	98.73
28	C. 16	Young on bottom of old plant	2.10	25.75	36.96	63.33	96.42
<i>Nereocystis luetkeana</i>							
29	C. 17	Old plant	2.15	33.60	54.88	90.23	100.31
31	C. 19	Very old plant	1.58	31.36	50.40	31.65	91.77
<i>Macrocystis pyrifera</i>							
33	C <sub>1</sub>		1.93	28.00	47.04	82.90	100.10
33	C <sub>2</sub>		1.56	24.64	31.36	91.37	99.49
37	C <sub>1b</sub>		0.79	19.60	25.76	70.88	95.82
38	C <sub>1c</sub>		0.66	16.24	24.64	81.31	97.84
39	C <sub>1d</sub>		0.67	18.48	26.88	84.65	98.18
40	C <sub>1e</sub>		0.54	13.44	19.04	80.01	99.33
Average.			1.87	29.81	47.41	81.25	95.84

A. Total nitrogen (N) analyses by T. C. Trescott, Bur. of Chem.

B. By official alkaline permanganate method.

C. By using one-half the amount of sample as prescribed by the official method.

D. By using 1 gram of sample and 3.25 grams of alkaline potassium permanganate.

E. By using 1 gram of sample and 5 grams of alkaline potassium permanganate.

necessary to supply 50 mg. of nitrogen will be 2.5 grams. Of this amount 1.5 grams are organic matter. That all this organic matter was not oxidized is evident from the fact that in all the experiments conducted under this method the supernatant liquids after digestion were colorless.

In some unpublished results obtained by Mr. A. R. Merz and Dr. W. H. Ross, both of the Bureau of Soils, it was found that a considerable amount of the nitrogen in kelp was water-soluble. Mr. Merz in his experiments treated the leaves, stems and whole plant with two successive portions of water. These were allowed to stand for 48 hours. He then filtered and analyzed the filtrates and residues. The results are given in Table II:

TABLE II—(PERCENTAGES)

No.	Description	Total nitrogen	Water-soluble	Per cent of total
1.....	Leaves	2.70	1.10	40.74
2.....	Stems	1.70	0.40	23.53
3.....	Plant	1.10	0.20	18.18
4.....	Plant	2.04	0.58	26.96
5.....	Plant	1.58	0.35	22.17

Dr. Ross in his experiment placed some leaves in a bomb and heated over night at a temperature of 190° which gave a pressure of about 17 atmospheres. By this treatment the slimy organic matter was coagulated so that it could be readily filtered: After filtration the nitrogen was then determined in the filtrate and residue. His results are given below:

TABLE III		
	Per cent of total material	Per cent of total nitrogen
Soluble.....	0.78	57.77
Insoluble.....	0.87	42.23

It is interesting to note that in Table II the per cent of water-soluble nitrogen closely approximates the availability percentages given in Column B, Table I, while in Dr. Ross' experiment the per cent of water-soluble nitrogen was considerably more.

In the next set of experiments one-half of the amount of sample as prescribed by the official method was

used. In other particulars the procedure was the same. Under those conditions the percentage of availability was considerably increased. The averages reached 47.41 per cent as against 29.81 per cent in the official method. Likewise the supernatant liquids were colorless.

Further experiments were made in order to determine whether or not more nitrogen was made available by using a larger amount of potassium permanganate. The results in Column D, Table I, were obtained by using 1 gram of sample with 3.25 grams of alkaline potassium permanganate. The average percentage of availability under these conditions was 81.25 per cent. That there was yet insufficient potassium permanganate present to effect complete oxidation was evidenced by the fact that the supernatant liquids were colorless.

In the next set of experiments, 1 gram of the sample was treated with 5 grams of alkaline potassium permanganate. It will be observed that the results here obtained approach 100 per cent and in a few cases are slightly over it. Where the higher percentages prevail the supernatant liquid after digestion was colored while in the others there was just lacking a sufficient amount of potassium permanganate to give the solution a permanent color. Judging from these results it appears that with enough potassium permanganate present to oxidize all the organic matter, all, or nearly all of the nitrogen in kelp is found to be available.

#### SUMMARY

I—The official alkaline permanganate method is not suited to determining the available nitrogen in kelp.

II—By using increased amounts of potassium permanganate the percentage of availability is increased.

III—By using a sufficient amount of potassium permanganate to oxidize all the organic matter present, all, or nearly all of the nitrogen is found to be available.

FERTILIZER INVESTIGATIONS, BUREAU OF SOILS  
U. S. DEPARTMENT OF AGRICULTURE, WASHINGTON



# LABORATORY AND PLANT

## PITOT TUBES FOR THE MEASUREMENT OF GAS VELOCITIES<sup>1</sup>

By ANDREW M. FAIRLIE

The need for an accurate method of determining the velocities of moving gases in pipes and flues is receiving increased attention from the marine and mechanical engineers, and it is a need which has long been felt by the chemical and metallurgical engineers, but has been somewhat neglected by them. Gases are used as raw materials, or appear as either intermediate or final products, in many chemical and metallurgical processes of manufacture.

Undoubtedly, in such processes, an accurate means of measuring gas velocities would lead to the prevention of much loss and waste, through the substitution of known facts for guess-work. For example, wherever air is used under pressure, as in the copper blast furnace or the copper converter, a knowledge of the amount of air used, in comparison with the theoretical amount required, would in many cases lead to a reduction of air, and so of power, wasted. In the sulfuric acid industry, where gas is diverted to two or more absorption towers connected in parallel, a knowledge of the velocity, and hence of the quantity of gas going to each tower would lead to a proper adjustment of dampers so as to secure equality of distribution and more economical operation. In suits for damages claimed to have been caused by obnoxious fumes escaping from the flues of industrial works into the atmosphere, the substitution of knowledge as to the quantity of escaping fumes, for estimates and guesses, would eliminate legal controversies. The business of selling natural gas and manufactured gas for power, heating and lighting, demands an accurate means of measuring the velocity of flow, in order to properly affix costs and selling prices. In designing the equipment of chemical and metallurgical plants, some means of calibrating the capacities of blowers and ventilating machines, vacuum pumps, aspirators, etc., would enable engineers to check up the claims of manufacturers of such equipment, and would prevent the installation of inefficient devices, as well as the financial losses involved thereby. Other examples of the value of a reliable means of measuring the velocities of gases will occur to the reader.

Georg Lunge states<sup>2</sup> that as early as 1866 Fletcher's modification of Pécelet's differential anemometer was described. This is in effect a crude sort of pitot tube. The velocity of the gas was calculated on the basis of the difference between the pressures, as measured by a manometer, exerted by the current of moving gas on two tubes, one of which was straight, the other being bent at a right angle, and turned so that the current of gas would blow into it. In using this anemometer, it was to be inserted into the air current to the extent of about one-sixth of the diameter of the flue.

<sup>1</sup> Presented at the 49th Meeting of the American Chemical Society, Cincinnati, April 6-10, 1914.

<sup>2</sup> Geo. Lunge, "Manufacture of Sulfuric Acid and Alkali," 3rd Ed., Vol. I, Part 1, p. 563.

The velocity at this point was assumed to be nearly equal to the average, and the velocity was based on a reading taken at this one point. Lunge admits that the accuracy of the assumption is doubtful, and adds: "There are no means at present<sup>1</sup> known of measuring the absolute quantities passing through a flue of any considerable sectional area with any degree of accuracy."

Since 1903 numerous investigators have published accounts of the results of their work on pitot tubes. Different forms of pitot tubes have been designed, each designer claiming for his form, perhaps, superior accuracy. With so many different forms of tubes, none acceptable as a standard, engineers were as badly off as if there were no pitot tubes at all, and, in fact, all forms of pitot tubes were more or less distrusted.

In September of last year, the results of an exhaustive series of comparative tests of the different forms of pitot tubes were published by W. C. Rowse.<sup>2</sup> Thanks to the painstaking work of this investigator, it is now possible to separate the wheat from the chaff, and a form of pitot tube may now be selected with some confidence. Those interested in the velocities of gases cannot do better than read the whole of the paper by Rowse, which, with diagrams, tables, etc., covers about fifty pages. With the consent of the author, to render his paper of still greater value, two errors in the statement of formulas which inadvertently crept into his work are here pointed out. On page 1343, paragraph 46 (*h*) reads as follows:

"It appears that an approximate relation exists between the mean velocity head of a gas flowing through the pipe and the velocity head found by placing the tube at the center of the pipe. For a 12-in. galvanized iron pipe results within 2 per cent may be expected from using the formula

$$\text{where } v = \sqrt{(2g)(0.80) h_c}$$

*v* = velocity in feet per second.

*g* = 32.2 ft. per second per second.

*h<sub>c</sub>* = velocity head in in. of gasoline at the center of the pipe obtained in a correct manner."

This is all correct except the value given to *h<sub>c</sub>*, which should read:

*h<sub>c</sub>* = velocity head in feet of gas flowing at the center of the pipe, obtained in a correct manner.

Again, on page 1372 (paragraph 76) a formula is given which reads:

$$h = 144s/pH,$$

where

*h* = velocity head in feet of air.

*s* = sp. gr. gasoline.

*p* = weight of water in pounds per cu. in. taken from Chart G.

*H* = velocity head in in. of gasoline as given in columns 18 or 19."

<sup>1</sup> 1903.

<sup>2</sup> J. Am. Soc. Mech. Eng., Sept., 1913.

This formula should read

$$h = \frac{144s\rho H}{w}$$

where

$w$  = weight of 1 cu. ft. air under existing conditions, and  $h$ ,  $s$ ,  $\rho$ , and  $H$  have the values assigned above.

I have been requested by the author to refer also to the third error in the paper, viz., Chart A, Appendix No. 3. Inclined dotted lines should be designated as follows, beginning at the bottom: 1/10; 6/100; 5/100; 4/100; 3/100; 2/100; 1/100; 1/200.

From this paper it appears that the most accurate form of the pitot tube is the standard tube of the American Blower Company, which was developed by Chas. H. Treat. After the publication of Rowse's report, the American Blower Company issued a special bulletin, entitled "The Pitot Tube and Fan Testing."<sup>1</sup> This Bulletin, which can be obtained gratis from the American Blower Company, Detroit, Mich., gives a dimensioned sketch of the pitot tube adopted by them as a standard, and reviews to some extent the work of Rowse. Some formulas for calculation are also given. The Bulletin is of some value, but the calculations and formulas given must be accepted with caution, as a number of errors have been noted, particularly in the first edition. Curiously enough, one of these errors is again in the value of " $h$ " (see above), the velocity head in feet of air. On page 25 of the Bulletin<sup>2</sup> the second equation given reads:

$$h = \sqrt{\frac{62.3p}{12w}}$$

where  $p$  = velocity pressure in inches water gauge.

$w$  = weight of one cu. ft. of air, under existing conditions."

The radical sign in the equation should be omitted.

On the same page it is stated (second line from the bottom) that  $v$  = velocity of air in feet per second, as applied to the various equations given on that page. In the fifth and sixth equations, however, the value of  $v$  is, in fact, the velocity of air in feet per minute. In the fifth and sixth equations, therefore, the symbol " $v$ " should be replaced by " $v_m$ ," to represent the velocity of air in feet per minute.

There are also evidently some errors in the formulas given on page 26 of the early edition of the Bulletin.

Reverting now to the consideration of the work of Rowse, the most important of his conclusions are:

1—The pitot tube as a means of measuring gases is reliable within approximately 1 per cent when the static pressure is correctly obtained and when all readings are taken with a sufficient degree of refinement; in order to obtain this degree of accuracy the pitot tube should be preceded by a length of pipe 20 to 38 times the pipe diameter in order to make the flow of gas as nearly uniform across the section of the pipe as possible.

2—All the methods of obtaining the dynamic head used in his experiments gave accurate results. Of

the methods of obtaining the static pressure by means of the pitot tube, the most reliable and accurate is by means of a very small hole in a perfectly smooth surface, as in the standard tube of The American Blower Company.

3—It appears that an approximate relation exists between the velocity head found by placing the pitot tube at the center of the pipe, and the mean velocity head of the air flowing. (See formula for a 12-inch pipe on page 583.)

From these conclusions it is apparent that there are limitations to the uses to which the pitot tube can be put. To extend these limits, further work will be required. There are many pipes already constructed in which it would be desirable to measure the speed of the moving gases, but which do not present a length twenty times the pipe diameter. How shall we determine the velocities in such pipes?

Rowse has given a convenient formula (conclusion "3" above) for arriving at approximate velocities from a single pitot tube reading taken at the center of a pipe 12 inches in diameter. Who will develop similar relations for pipes of other sizes?

That such relations for different sizes of pipes are desirable is evident to any who have gone through the laborious work of taking 20 pitot tube readings across two diameters of a pipe in order to obtain a single mean velocity head. Some have attempted a short cut method by using, for obtaining the dynamic pressure, a tube long enough to reach entirely across the pipe containing the gas whose velocity is to be measured, with a number of small holes (centers all in the same plane) bored in the tube, each hole being at the center of one of the annular zones of equal area into which the cross-sectional area of the pipe is assumed to be divided, and all of the little holes being turned so that the current of gas will blow directly into them. Another short cut device which is sometimes used for obtaining the dynamic pressure consists of a number of tubes of different lengths, each with the inside end bent at a right angle towards the gas current, the inside end of each being located in the center of one of the several annular zones into which the cross-sectional area of the pipe is mentally divided, and the outside end of each being connected to one common manifold pipe, where the inequalities in the various pressures exerted on the several tubes are neutralized. With either of these devices it is assumed that the dynamic pressure tube gives a mean dynamic pressure for the entire cross-sectional area of the pipe, from which, by deducting the static pressure, the mean velocity head of the gas can be obtained. However, since the velocity of a current of gas does not vary directly as the velocity head, it is difficult to see how such instruments, which give as net result a straight average of the velocity heads at the different points in the pipe tested, can be expected to produce data on which to calculate a correct mean velocity. From the formula

$$v = \sqrt{2gh}$$

the velocity varies as the square root of the velocity head. To obtain a correct mean velocity, a correct

<sup>1</sup> Bull. 35, Series 1, January, 1914.

<sup>2</sup> It is understood that in the later editions of the Bulletin, most of the errors have been corrected.

mean velocity head is needed; and to obtain a correct mean velocity head it is necessary to average the square roots of all the velocity head readings taken, throughout the cross-sectional area of the pipe, and then to square the average.

There is at present no royal road to obtaining accurate velocity measurements by means of the pitot tube. Investigators, to obtain accurate results, must have recourse to the painstaking methods adopted by Rowse. We are told that, for a 12-inch pipe, results within 2 per cent of correct may be obtained by using 0.8 of the velocity head in feet of gas at the center of the pipe. Lacking similar factors for pipes of other sizes, velocities must be calculated from readings taken at numerous points in the cross-sectional area of the pipe.

In recapitulation, it may be observed that:

I—As a result of the work of Rowse, engineers may now select a type of pitot tube which may be used, under certain conditions, with confidence.

II—Further investigation needed, to render the pitot tube more generally available as a means of measuring gas velocities, includes:

1—A means of determining accurately the velocity of gases in pipes whose length is less than 20 times the diameter.

2—The establishment of definite relations between the velocity head at the center of a pipe, and the mean velocity head, for pipes of various sizes and shapes.

NOTE—I am indebted to the author of the original paper which constitutes the basis for this one—Mr. W. C. Rowse—for his courtesy in reading this manuscript, and for valuable suggestions offered by him and adopted herein.

COPPERHILL, TENNESSEE

## THE NON-UNIFORMITY OF DRYING OVEN TEMPERATURES

By LORIN H. BAILEY

Received April 13, 1914

While testing the accuracy of the heat control of a new electric drying oven, it was observed that there

In the above tests only those thermometers were used which had been standardized by the Bureau of Standards. With ovens having glass doors the thermometers were placed on the shelves and the temperatures read by making the observations through the glass in the door without opening the oven. With the other ovens the following scheme was adopted: Six 50 cc. Erlenmeyer flasks were filled with clean, dry sand, stoppered, and through the stoppers the thermometers were inserted so that the bulbs were held in the middle of the flasks. These flasks with their thermometers were then placed in the various positions in the ovens and after having remained there long enough to come to equilibrium they were removed and the thermometers read as quickly as possible. While this method is not absolutely accurate, it is sufficiently so to indicate whether or not there is any great variation in temperature.

After testing these various drying ovens the writer's attention was called to an article to R. G. Grimwood<sup>1</sup> on the "Analysis of Crude Glycerine by The International Standard Methods, 1911." In this article the author mentions difficulty when using a drying oven which complies with the International Standard Methods specifications and which shows a maximum variation of 16° C. on one shelf and between the two shelves a maximum variation of 45° C. He then describes a special electric drying oven which has proved satisfactory for drying glycerin. This oven showed a maximum variation of 2.2° C. from 160° C., the temperature desired. The results shown by Mr. Grimwood are very much better than the writer was able to obtain with any oven not surrounded by boiling water and steam.

The results in the above table show that elaborately designed and expensive ovens are no more reliable than the most simple and inexpensive ones. Of the ovens tested, only those surrounded by boiling water and steam are capable of maintaining even approximately uniform temperatures.

I wish to thank Dr. J. A. LeClerc for his interest

No.	Kind of oven	Reading of thermometer	Maximum range of temperature on		Maximum variation	Approximate dimensions inside
		inserted through top of oven °C	top shelf °C	lower shelf °C	on both shelves °C	
1	Electrically heated and controlled.....	107	99-114	99-108	24	12 × 12 × 14
2	Electrically heated and controlled.....	105	89-100	88-103	15	12 × 13 × 18
3	Electrically heated and controlled.....	103	94-104	89-102	15	9 × 9 × 15
4	Gas heated porcelain lined.....	90	88- 92	92-102	14	11 × 12 × 16
5	Gas heated air jacketed.....	100	94- 96	105-118	24	8 × 10 × 11
6	Gas heated constant level water and steam jacketed.....	98	96- 98	95- 98	4	13 × 15 × 15
7	Steam jacketed.....	100	101-101	101-102	2	15 × 8 in. diam.
8	Gas heated constant level water and steam jacketed vacuum oven.....	100	100-100	100-100	0	15 × 8 in. diam.

was a wide range of temperature in different parts of the oven, not only between different shelves but also between different positions on the same shelf. Ordinarily the temperature recorded on the thermometer inserted through the top of an oven is taken as the temperature at which the drying is made, but it was seen that such could not be done with this particular oven. Following this observation a number of different types of drying ovens were tested as to their uniformity of temperatures throughout the drying chambers. The variations in temperature are shown in the accompanying table.

and suggestions in connection with the testing of these various ovens and the writing of this report.

LABORATORY OF PLANT CHEMISTRY, BUREAU OF CHEMISTRY  
U. S. DEPARTMENT OF AGRICULTURE, WASHINGTON

## A MANOSTAT FOR USE IN GAS ANALYSIS

By HARVEY N. GILBERT

Received April 14, 1914.

In the combustion of gases confined over mercury in a combustion pipette, more or less difficulty is always experienced by the operator in avoiding a difference of pressure due to the difference of level between that

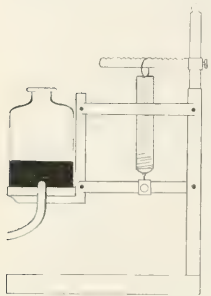
<sup>1</sup> J. Soc. Chem. Ind., 32, 22.



of the mercury in the pipette and that in the level bulb. This is ordinarily accomplished by resting the level bulb on a pile of blocks which can be removed or added to as may be necessary. But these blocks are inconvenient and usually they are thick enough to cause considerable difference in the level of the mercury. Furthermore, the abrupt changing of the pressure may cause leakage in the rubber connections and may lead to explosions in cases where the rapid lowering of the pressure in the pipette during the progress of a combustion causes the gas to enter the pipette too rapidly.

The following apparatus is designed to overcome these difficulties by maintaining a constant level of the mercury during the combustion, thus insuring

*constant pressure.* The device shown in the accompanying figure consists of a metal base and an upright which supports parallel lever arms. At the ends of these arms is attached a pan which moves vertically, but always remains in a horizontal position. The level bottle is connected as usual with the combustion pipette by means of rubber tubing and it is placed upon the pan. A coil spring is suspended from the upper part of the framework and is attached to an adjustable point on the lever arm.



By moving the point of support of the spring on the lever arm it can be so adjusted that the vertical distance through which the pan moves, when the spring is deflected, is just equal to the height of the column of mercury which has left the pipette in order to produce this deflection.

The principle is rendered clearer if one considers the level bottle suspended directly on a spring. A unit weight of mercury produces an elongation of the spring which is just equal to the height of this amount of mercury when it is confined in the pipette. Thus the level of the mercury is automatically kept constant during the entire combustion.

The above form of the apparatus was designed in order to make it possible to use different sizes of level bottles and pipettes, and also to make it easy to replace the spring by others of different strengths. Economy of space was another reason for adopting this form. While this form is not mathematically exact, as is the case of the freely suspended spring, it maintains a pressure which is constant for all practical purposes. The apparatus can also be made to maintain a constant pressure either above or below that of the atmosphere, by adjusting the spring as described before.

The principle is capable of other applications to apparatus for handling and measuring gases.

The apparatus is manufactured by Greiner and Friedrichs, Stützerbach in Thüringen, Germany, and is known as the "Gilbert Manostat."

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## ADDRESSES

### THE EXCESSIVE QUANTITIES OF NITRATES IN CERTAIN COLORADO SOILS

By WM. P. HEADDEN

Received April 21, 1914

The Colorado Experiment Station has issued, up to the present time, eight publications<sup>1</sup> pertaining to the occurrence and origin of excessive quantities of nitrates in certain soils. These remarkable occurrences were first definitely recognized about 1905. The difficulty of accounting for the nitrogen necessary to form these nitrates presented itself from the very first, but no other theory than the fixation of atmospheric nitrogen seemed available and adequate.

The above mentioned publications report the occurrence and distribution of the nitrates and their effects upon vegetation, particularly upon apple trees, but also upon the quality of sugar beets. The source of these nitrates is sought in the activity of the bacterial flora of the soils. This view is urged on the ground that there is no known source from which the nitrates may be derived ready formed. The distribution of the nitrates is such as to preclude their derivation from any system of rocks, and they are so widely distributed that some generally prevailing condition must be operative in their production. The direct evidence adduced consists of a series of consistent facts which support this contention; *i. e.*, these soils have been shown, by direct experiment, to fix nitrogen in a marked degree, and also to change it into nitric acid (nitrates) very much more energetically than do eastern, southern and foreign soils in general. The fixation is attributed to the azotobacter which are found to

occur in these soils in great abundance, and whose characteristic pigment constitutes the first most striking character of these niter-areas. The appearance of this color has been recognized very generally by the orchardists and ranchmen as the beginning of serious trouble. It is related throughout these publications that complaints were made that the land turned brown and then the trees died, or that nothing would grow.

The very first occurrences examined had been mistaken as exudations of oil. The surface of the ground was black and glistening. The areas involved were small and nearly circular. An analysis of the surface soil showed the presence of 13.4 per cent of water-soluble material, of which nearly 42.0 per cent consisted of nitrates. These were largely the calcic and magnesian salts. There was a number of such brown areas, mostly smaller than the one referred to, in this locality. That such areas should be destitute of vegetation would seem a natural and even necessary result of the presence of such quantities of nitrates, in this case 5.6 per cent of the air-dried soil. Other and larger areas were observed, which were either devoid of vegetation, or on which the vegetation was suffering without the presence of any evident cause. Examination of such cases showed the presence of unduly large amounts of nitrates. These facts enlarged the question from one of scientific curiosity to one of very great agricultural importance. Individual orchardists had, in the meantime, taken cognizance of the fact that this was a serious trouble and that there was an intimate connection between the turning brown of the soil and the death of the vegetation, whether orchard trees, alfalfa or vegetables. Complaints of "brown-spots on which nothing will grow" became quite numerous and pointed the way to new localities for these

<sup>1</sup> *Bulls.* 155, 160, 178, 183 and 186, by Wm. P. Headden; 179 and 193, by Walter G. Sackett; 184, by Walter G. Sackett and W. W. Robbins.

occurrences. More than thirty cases are presented in detail to establish the fact of the occurrences of nitrates in these soils, and to give the conditions under which they occur, together with their distribution throughout the State.

In regard to the quantities of nitrates present, they are shown to vary from a few tenths of one per cent to upwards of six per cent of the air-dried soil. The areas involved vary from a few square feet to many acres in a single body. The distribution of these areas is practically throughout the cultivated sections of the State, but they are much more common in some sections than in others.

#### EFFECT OF NITRATES ON TREES

These occurrences of nitrates were not always present in the localities where they are now found. While some of them were known eighteen and twenty years ago, their real nature was unknown, and they did not become very prevalent till 1908 or 1909 when their effects became so pronounced that they could not be overlooked. These results were disastrous and very noticeable because in 1909 apple trees began to succumb—at first a few trees here and there, two, four or a dozen—but this was rapidly followed by the dying of hundreds in a body, taking, in some cases, the whole of small orchards. The cause seemed evident, but had to be proved, which was done by the application of sodium nitrate to comparatively small trees, four-year-old ones, when it was found that all the changes observed in the affected trees were reproduced by the nitrate, even to the killing of the trees. As no data were at hand showing the effects of sodium chloride on trees, this too was tried, because this salt is sometimes, but not at all often, present in considerable quantities in Colorado soils. Sodium chloride did not produce any of the phenomena observed in the orchards. These results were so conclusive in regard to the cause of the death of the apple trees, that no reasonable doubt remained in regard to it. The beginning of this serious feature is given as 1908 or 1909. It continued to spread and to increase in virulence until in 1910 and 1911 it was so prevalent that the area actually treated of in *Bull. 178* is given as four hundred acres and the affected area as from three to four hundred square miles. In one district, including about fifty square miles, the orchards have been ruined, at least practically so, as very few healthy orchards survive.

No statement is anywhere made indicating the minimum amount of nitrates capable of injuriously affecting apple trees or other vegetation; it is merely shown that the application of five pounds of nitrate, sodium nitrate, to a four-year-old tree produced some injury. On the other hand, it is shown that the spread of the roots of a medium sized apple tree is not less than forty feet and that in many cases the nitrates occurring within a radius of twenty feet of the tree trunk amount to as much as several hundred pounds, quantities very much in excess of those experimented with and which sufficed to do injury to, and even to kill, the trees.

The progress of the injury to orchards is shown to be remarkably rapid. An instance is given in which the injury began to become evident in May and by August about two acres of the orchard had been killed; by the end of November, nearly three acres and within a year thirteen acres were in such bad condition as to be of little or no value. This land had become mealy and then brown and the amount of nitrates formed and brought into the feeding areas of the roots passed the danger point and the trees died.

The amount of total nitrogen present in the brown spots is, as a rule, larger than is commonly present in Colorado soils which does not usually exceed 0.10 per cent, and is furthermore largely present in the form of nitric nitrogen. It is not uncommon to find the nitric nitrogen equal to from 15 per cent up to even 90 per cent of the total nitrogen. The contrast between the amount of both total and nitric nitrogen in the brown spots and the ordinary soil is often very great. An example is given in which the brown spot contained 6629.6 p. p. m. total, and

6444.5 p. p. m. nitric nitrogen, while a sample taken twenty feet from this, but outside of the brown spot, carried 435.2 p. p. m. total and 2.0 p. p. m. nitric nitrogen; the soil was not wet in either place. In another case the brown spot contained 8,500 p. p. m. total and 7,077 p. p. m. nitric nitrogen while the ordinary soil sixteen feet from the edge of it carried 591.6 p. p. m. total and 16.0 p. p. m. nitric nitrogen. The brown color is characteristic of these spots and also of old azotobacter colonies. The excessive nitrogen in the soil, especially the excessive nitric nitrogen, is very definitely indicated by the color of the surface soil, and in cases in which the accumulation of nitrates is not too great these soils teem with azotobacter.

#### NITRATES AND COMPOSITION OF SUGAR BEETS

These occurrences are looked upon as exaggerated instances of a general condition frequently prevailing in Colorado soil. It is cited as a fact that the quality of the sugar beets grown in the Arkansas Valley from 1893 to 1904 averaged 17.5 per cent sugar and worked easily in the factory, but from 1904 till 1911 the beets averaged much lower in sugar, 14.2 per cent in 1910, and worked very badly, yielding as high as 9.5 per cent molasses. During this period there were some excellent beets produced every year, but not enough to maintain the average above the figure given. The fact that fields of most excellent beets, containing 18–23 per cent sugar, were produced annually throughout the Valley was taken as a refutation of the frequently made claim that it was all due to climatic conditions. The low general average for the sugar content, the bad working qualities, and the large percentage of molasses produced were interpreted as indicating some prevalent soil condition which produced this effect. The prevalent soil condition was believed to be the presence of too large a supply of nitric nitrogen, *i. e.*, nitrates, during the season. The whole subject of the deterioration of the quality of these sugar beets is considered as an illustration of a general effect upon a crop due to an excessive supply of nitrates furnished by the soil itself.

Some of the more specific facts adduced in this connection are that the beets grown in this Valley contain high percentages of nitric nitrogen, or nitrates. It is shown that some samples of very poor beets carry from 0.13 to 0.6 per cent of nitrates calculated as potassic nitrate, whereas the best beets analyzed contain none. The molasses produced contained large amounts of nitric nitrogen, from 0.12 to 0.47 per cent, or from 8.64 to 33.84 per cent of nitrates calculated as potassium nitrate, as compared with 0.046 per cent of potassium nitrate in the best Bohemian molasses analyzed.

Starting from these facts and guided by previous field observations, a study of the effects of nitrates upon the composition of the sugar beet and its working qualities established the fact that the composition of beets grown with the application of sodium nitrate in excessive quantity was just such as was actually found for the general crop including the low percentage of sugar, *i. e.*, the presence of nitrates in the beets, the watery-white, brittle flesh, and the production of thick juices having a low coefficient of purity.

The poor quality of the beets during the period mentioned had often been attributed to the attacks of the fungus *Cercospora beticola*, or leaf-spot. The attacks of this fungus were so severe and general that it had to be considered. The foliage on whole fields of beets had often been practically destroyed. In the absence of any data to show that any further injury than that of defoliation is ever produced by this fungus, the effects of total defoliation were studied. It was found that total defoliation as late as September 6th, profoundly affected the composition and total crop of beets. The changes produced in these beets, however, were almost entirely different in kind and degree from those produced by the application of nitrates. These latter changes were much more profound than had been indicated as probable by a study of the beets from 127 fields where the fungus attacks varied in virulence from very light to the almost total



destruction of the leaves. The chief points which it was endeavored to establish, were: (1) Are the changes produced in the composition of the beets by defoliation, whether by knife or leaf-spot, identical in character with those found in the deteriorated crop? (2) Are the changes the same as those produced by the application of large quantities of nitrates? It was found that both defoliation and nitrates produce great changes in the beets and their qualities, but that the beets grown with the application of nitrates show those changes which were found in the deteriorated crops, while the defoliated beets do not. A widely distributed and uniform cause is inferred as producing these results, the immediate expression of which is the presence of nitrates in excessive quantities or at a time when they seriously affect the quality of the crop.

The occurrence of very large, exceptionally large quantities of nitrates has been established by direct observation in many localities and by a large number of analyses. The effects of such excessive quantities of nitrates upon apple and other trees, and vegetation in general, have been observed in many localities, and the sufficiency of the nitrates to produce the effects observed in the case of apple trees established by direct experiments made on young trees.

The general and more diffused effects, as well as the wide distribution of the cause itself, have been established by a study of sugar beets, their composition and characteristic deportment in the preparation of sugar from them.

The problem just stated presented considerable difficulties because of the many factors involved, the most patent of which may be enumerated as the part played by: (1) excessive salts in the soil, *i. e.*, alkalis; (2) excessive water and seepage (generally associated); (3) the effects of various plant diseases, *e. g.*, leaf-spot; (4) insect injuries; and (5) all of the various effects suggested by that comprehensive term "climatic conditions."

A previous study of the effects of the first two, extending over a period of four years, led to the conclusion that these factors may well be completely eliminated, so far as the questions here presented are concerned. The effects of the leaf-spot have been specifically studied in this connection, and while its seriousness is in no way minimized, it is not considered as the cause of the specific deterioration. Those factors signified by the term "climatic conditions" are in part recognized, but the most of them are considered as too general to admit of definite study under such a designation. Hail, in one case was practically fatal to a crop while in another its effects were inappreciable; the influences of dry weather, hot winds, early or late frosts, etc., were also considered. Conditions for their study were most favorable during the whole of its progress which extended over three seasons.

#### EFFECTS OF COMMON FERTILIZERS

Still other factors which had to be considered pertained to the soil, its mechanical, and especially its chemical properties; also its supply of plant food, and the ratio of the respective nutrients to one another. These influences could not be studied satisfactorily by any analytical method, therefore experiments to determine the effects of the common so-called plant foods, singly and in a variety of combinations, were depended upon for information. Analyses showed an abundance of calcium, magnesium, potassium and phosphorus, together with a fair amount of nitrogen. The plant foods added in the experiments were stockyard manure, calcium as burnt lime and as factory waste lime (which contains both phosphorus and nitrogen); nitrogen as sodium nitrate, phosphorus as superphosphate, and potassium as sulfate or muriate. The results were concordant with previous observations made on the effects of fertilizers applied to Colorado soils, *i. e.*, they produced no marked results, such as would reward one for applying them, and what was more significant, no one of them effected so definite an improvement in the quality of the beets as to be unquestionable, or even to indicate a probable line of experimentation for the betterment

of the quality of the crop. In one series of experiments the addition of 250 pounds of sodium nitrate per acre increased the crop and improved the quality. All quantities in excess of 250 pounds per acre lowered the yield and depressed the quality.

In these fifty odd experiments, just referred to, not a single positively beneficial result was obtained. It was concluded that there was no lack of available plant food and no disadvantageous ratio which was corrected by any fertilizer or mixture of fertilizers used. Of the elements in question in this connection, potassium and phosphorus are not variable from time to time, but the nitrates have long been known to be. There are portions of the land on which these experiments were made in which very excessive quantities of nitrates developed at times. The assumption is tacitly made, though not stated with definiteness, that the disturbing factor in these experiments was the formation of a sufficient quantity of nitrates during the season to eliminate the differences which one would expect to be produced by the various mixtures of fertilizers applied, so that the result was the production of very uniformly poor beets. These experiments extended over two years and the results are concordant with those obtained in other experiments.

It is stated as a general proposition that the Colorado soils are only moderately well supplied with nitrogen, the average being 0.10 per cent. On the other hand, it is also stated that nitrogen-hunger has not yet been observed; on the contrary there is everywhere evidence of an ample supply, often positive evidence of an excess, though not to the extent of causing injurious effects, such as the burning and killing of plants. In this connection emphasis is constantly laid upon the high ratio of nitric nitrogen to the total, quite frequently reaching the high figure of 50.0 per cent, or even higher, while the usual maximum for this ratio is given as 5.0 per cent.

The amounts of nitric nitrogen which occur in many places, involving large areas, where orchards and other vegetation have been injured or killed outright, have already been given, but the quantities occurring in cultivated lands, apparently in good condition, but which produce sugar beet crops of poor quality were also studied and compared with those in other soils. The maximum amount of nitric nitrogen occurring in ordinary soils is assumed not to exceed 8 p. p. m. The average amount found in 71 samples of a Fort Collins soil taken to depths of 2 and 3 inches, October 4-8, was 6 p. p. m.; of 28 samples taken from the third to the sixth inch inclusive, was 5 p. p. m. The average of 46 samples taken to a depth of 6 inches from different beet fields, October 1-15, was 20 p. p. m.; from 54 other beet fields, also taken to a depth of 6 inches, January 26-31, was 13 p. p. m. The abundance of nitrates in some of these samples does not appear at all when the results are given as averages which merely show that the first 46 fields sampled contained, in early October, 2.5 times as much nitric nitrogen as is usually considered a maximum quantity. Among these 46 samples is a maximum of 160 p. p. m. or twenty times the usual maximum. Others contain 70, 80, 100 and 120 p. p. m., respectively, and among the 54 samples taken in January, a maximum of 140 p. p. m. occurs.

#### SODIUM NITRATE APPLIED TO SOILS

In the experiments with sodium nitrate it was found that all quantities in excess of 250 pounds per acre produced beets showing the qualities of the crops of deteriorated beets. The time of application or occurrence of the nitrates is evidently of considerable importance, but leaving this out of consideration, the general result was that the deterioration in the beets increased with the increase of the amount of nitrates added till 1000 pounds per acre was reached, which produced the maximum depression in the quality of the crop obtained. This maximum depression may be indicated by the percentage of sugar, which was depressed from 16.5 to 11.0 per cent, or 5.5 per cent of the beets, and the ratio of protein to the total nitrogen which was reduced from 31 to 16.5. This is a reduction of 43 per cent in



this ratio, but the ratio of 31 is only a little more than 60 per cent of that of very good beets. The average amount of nitric nitrogen found in the surface 6 inches of these 46 fields corresponded to the presence of 480 pounds of sodium nitrate per acre while the 160 p. p. m. corresponded to about 1440 pounds. This quantity, however, is still very far from the maximum found in beet fields by systematic sampling. A certain field was chosen and divided into eight sections and sampled seven times during the season. The first samples were taken March 4, and the last August 25. During this period the respective sections into which the field was divided varied greatly in their content of nitric nitrogen not only among themselves but from date to date of sampling. The maximum variation in any one section was from 6.5 to 333 p. p. m.; another varied from 4.1 to 251 p. p. m.; the beets from this field were poor in quality, 12.6 per cent sugar. Another field sampled in like manner showed 130 p. p. m. as the maximum with the next highest sample, 67 p. p. m., but the nitrates throughout the season were low. The samples taken August 25 ranged from 2.5 to 12.0 p. p. m. and the beets were good—17 per cent sugar. The samples last referred to were taken to a depth of one foot, and gave a maximum of nitric nitrogen corresponding to approximately 8000 pounds of sodium nitrate for the surface acre-foot.

The question of the origin of these nitrates has been kept in view from the beginning of the work. The presence of the nitrates in many of the Colorado soils in very extraordinary quantities cannot be doubted, neither can it be doubted that the brown-spots with their remarkably large quantities of nitrates are exceptional manifestations of a condition that is met with over large areas and constitutes an important factor in the agriculture of the State.

#### WATERS NOT SOURCE OF NITRATES

The first source considered for the nitrates occurring in the brown-spots is a concentration of previously formed nitrates, but this is regarded as inadequate. Some of these spots are described as occurring isolated, or in isolated groups, on soils of lacustrine origin surrounded by granites and mica schists while the deeper waters are of very high purity and acid in quality. The surface waters are, as a rule, charged more or less heavily with the ordinary alkalis of the section, which consist of the sulfates of calcium, magnesium and sodium with relatively small amounts of chloride and carbonates. There is one exception to the absence of carbonates from the deeper waters. Nitrates are absent except in such quantities as may be found in waters generally, even in waters entirely free from contamination. The nitrate spots are not points of issue for underground waters. Further, the spots occur on mesas or small plateaus where there are no other streams than irrigating ditches. These irrigating ditches, with no important exceptions, carry water furnished by mountain streams, and such waters have not been found to carry nitrates. The ground waters of many sections of these districts have been examined and found free from nitrates, except in cases where the waters were taken from beneath areas the surfaces of which were rich in nitrates. Drain waters from alkaliized areas were also free from nitrates, unless the drains passed beneath nitrated areas. The alkalis, soils and ground waters occurring on or in lands adjacent to and higher than some niter spots, were examined in detail and no nitrates beyond traces were found, while samples of soil taken to a depth of one foot from the area discussed, showed the presence of two and a quarter tons per acre. This process of elimination of sources sufficient to explain satisfactorily the occurrence of these nitrate spots led to the rejection of the concentration theory.

There was no question about the presence of the nitrates in sharply defined areas with no apparent and adequate source of the nitrates. Many of these spots occurred on well drained land and the water that flowed from the higher lands in the gravel underlying these general sections contained only 0.10

p. p. m. of nitric nitrogen. The soils in general do not contain a large supply of nitrogen from which nitrate may be formed; their nitrogen content averages about 0.10 per cent. If this nitrogen were all nitrifiable and were nitrified practically at one time and converted into sodium nitrate it would give only about 0.60 per cent of this salt in the air-dried soil, whereas the brown-spots often contain very much more, so that the question relative to the source of the nitrogen became an insistent one. It seemed evident that as the soils themselves contained an inadequate supply for the formation of the nitrates found, and these nitrates did not exist ready formed in the alkalis and ground waters of adjacent lands, there was only one other adequate source and that was the atmosphere. But ordinary soil has no marked power, even when alkaline in reaction, to bring about the oxidation of atmospheric nitrogen either directly or indirectly. Certain soils may, as has been suggested, bring this about in a small measure, but not in such a marked degree as is presented in these spots. Some agent was sought which is capable of transferring the atmospheric nitrogen to the soil in some easily nitrifiable form. The predication of some such agent was considered as the only reasonable explanation for the facts, because in the beginning these spots were sharply defined and characterized by a brown color and an abundance of nitrates. While the limits of these spots were most sharply defined, they were not fixed; on the contrary, they often extended rapidly. The brown color and remarkable quantities of nitrates were always associated. This excessive development was a local one which extended its boundaries and was characterized by the presence of a brown color. These considerations led to the adoption of the theory of fixation, due to microorganisms. The azotobacter were known to be able to appropriate the atmospheric nitrogen in the building of the proteid material of their own bodies. Some of them, at least, were also known to form brown pigments. Given the presence of such organisms, the brown color of the spots was easily explicable, and with it the source of the excessive nitrogen, *i. e.*, the atmosphere, through the agency of these azotobacter. The presence of these organisms would account for the nitrogen and the color, but not for the final form of the nitrogen, *i. e.*, as nitrates. This transformation, however, is very rapidly brought about by other organisms. It was tentatively held that the azotobacter themselves effected this transformation, but this view was abandoned, because the reactions on which it was based were subsequently found to be due to the pigments formed by the azotobacter and not to nitrates.<sup>1</sup> It has quite recently been held by Mr. Dan H. Jones,<sup>2</sup> that the azotobacter form nitrates in their body tissues. If this were correct it might contribute materially in accounting for the formation of these nitrates. The reactions obtained by Mr. Jones, however, were very probably due to pigments and not to nitrates.

These soils were tested and it was found by experiments that they possessed, in a high degree, the power to fix nitrogen, and that this power is limited only by those conditions obtaining in the soils which limit the growth of the azotobacter themselves. It was also shown that these soils possess a very high power of nitrification.

The bacteriological and cognate features are treated of in *Bulls.* 179 and 193, by Professor Sackett and in *Bull.* 184, by Sackett and Robbins. Investigation of the soils from these standpoints developed the fact that all of the soils in question gave rise to remarkable developments of azotobacter, heavy films being obtained in a few days. Further, pure cultures of these bacteria fixed notable quantities of nitrogen and produced pigments freely. Some samples collected from the surface of

<sup>1</sup> The reaction of these pigments with phenolsulfonic acid render this reagent altogether unfit for the estimation of nitric nitrogen in some soils. Large quantities of the pigments give, with this reagent, a deep brown color which on sufficient dilution appears yellow with a tinge of brown—very easily mistaken for the nitric acid reaction.

<sup>2</sup> *Trans. Roy. Soc. Can.*, 3 (1913), Sec. 4.

the interior of these brown-spots failed to give a development of azotobacter, but samples from the deeper portions of them showed that the azotobacter were still living. They had merely been killed off in the upper portions. The azotobacter-flora of these spots were found to be abundant, and the high nitrogen-fixing power of such soils was reasonably explained. No definite attempt to account for the energy needed for the growth of the azotobacter was made. It was simply stated that some of the samples of soil preserved in a moist chamber in the light developed an abundant growth of algae, and this was suggested as a possible source of energy.

The ammonifying power and algal flora of some of these soils were subsequently studied by Sackett and Robbins. The results showed that these nitrate soils possessed a very much higher ammonifying power than the ordinary Colorado soils—two, and in some cases, three times as much. Colorado soils compared with soils from New Jersey, North Carolina, California and Iowa, exceed them in ammonifying power from one and one-half to eight times, except in cases in which lime had been added to a New Jersey soil. The results of the study of the algal flora present in the samples examined showed the presence of twenty-one different species of algae, nineteen of which belong to the *Cyanophyceae*. A few not present in the samples examined in this study have since been met with in other samples. A few samples of raw adobe soil have been found to be devoid of an algal flora and also of any power of fixation. The subsoils in some of the good cultivated lands are well provided with algal spores, probably through the instrumentality of earthworms, for they develop a strong growth of algae when exposed to sunlight in a moist chamber.

The last step taken in this work pertains to the nitrifying power of these soils. Experiments were made with samples of these soils early in the progress of this work in which gains in nitric nitrogen ranging from 19 per cent of the nitric nitrogen present at the beginning of the experiment to 138 per cent were recorded. The former figure, 19 per cent, was obtained in the original sample kept in the laboratory in its natural, moist condition; the 138 per cent gain was obtained on incubation at 28° C. for 48 days. A systematic study of this subject by Professor Sackett has been but recently completed. The results show that these Colorado soils have a high nitrifying power, especially for ammoniac sulfate and carbonate.

In comparison with foreign soils, *i. e.*, soils from other States, the Colorado soils have a far superior nitrifying power; *e. g.*, the average net gain of the positively reacting Colorado samples in the presence of ammonium sulfate was 672 p. p. m. of nitric nitrogen, while that of the foreign samples was 151 p. p. m. With ammonium carbonate the average net gain for the Colorado samples was 521 p. p. m., and for the foreign samples 215 p. p. m.; with dried blood this gain was for Colorado samples 432 p. p. m. and for the foreign samples 267 p. p. m. The significance of these results, showing the superiority of the Colorado samples over the foreign samples in nitrifying power, cannot be interpreted in any other way than as strongly supporting the views previously advanced.

The series of facts so far established seem conclusive in establishing the correctness of the view that the occurrence of these unusual quantities of nitrates in the Colorado soils is primarily due to fixation of atmospheric nitrogen by azotobacter.

It is held that these conditions suggest an explanation for the formation of the Chile-salt-peter beds, but the economic beneficence of these soils as a source of nitrates to be used as a fertilizer is held to be wholly impracticable.

#### SUMMARY

The basal facts in these investigations are:

- 1—The presence of very large amounts of nitrates in certain areas.
- 2—These areas are characterized by a brown color.

3—The quantity of nitrates in the areas is frequently sufficient to exterminate all vegetation and render the land barren.

4—The identity of the action of sodium nitrate upon apple trees with the action of the salts in these areas was established by direct experiment.

5—The general distribution of this occurrence has been recognized by its effects upon the composition and qualities of the sugar beet crop.

6—It has been established by extended field experiments that the composition and character of these crops are identical with those produced by the application of Chile salt-peter.

7—It has been shown that any theory of concentration of previously existing, ready formed nitrates by the agency of water is not adequate to explain the facts found, as the nitrates do not exist in the alkalis, soils or waters of these sections.

8—It has been established that these soils possess a high nitrogen fixing power.

9—Azotobacter occur very abundantly in these soils.

10—The azotobacter form a brown pigment which accounts for the characteristic color of the spots or areas.

11—The ammonifying power of these soils is very much higher than that of the ordinary soils.

12—Their nitrifying efficiency has been shown to be exceedingly high.

13—The algal flora of the soils has been found to be abundant and may furnish the energy necessary for the growth of azotobacter.

STATE AGRICULTURAL COLLEGE  
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## THE WORKINGS OF THE CALIFORNIA INSECTICIDE LAW<sup>1</sup>

By GEO. P. GRAY

We have in successful operation the National and State Food and Drug laws, intended to safeguard against fraud and imposition, the millions of human stomachs of the nation. The stomachs of domestic animals are protected in a like manner by the operation in many states of feeding-stuffs laws. Other states have been equally solicitous of the welfare of the automobile by passing oil inspection laws. Even the food of plants has not been overlooked and is regulated by many state fertilizer laws. And lastly, but not least (certainly in respect to the number of individuals affected), the crawling and creeping things of the earth have been the subject of National and State legislation to insure that they shall receive their full and unadulterated measure of the potent poisons which are dealt out to them so lavishly by the hand of man.

Inasmuch as the scientific study and application of insecticides and fungicides are of very recent development and the attempt to control the materials used for that purpose by legislation dates from the year of 1898, this matter has only recently come to the serious attention of chemists. Agricultural literature is full of information on the subject of insecticides but most of the work reported has been that of the entomologist whose training has been along other lines than chemistry. The rapid development of this line of work on a more scientific basis, the more intimate study of the action of poisons on insect and fungous life, has shown the need of chemical advice. The passage of control measures has also necessarily added to this need, there being at present not less than twelve states which have passed laws regulating the manufacture and sale of insecticides and fungicides and possibly other states not known to the writer. Other states will doubtless follow.

The examination of materials incident to the administration of these laws is largely a chemical problem. This, then, has opened up no inconsiderable field for chemists and will more and

<sup>1</sup> Presented before the California Section of the American Chemical Society, San Francisco, December 13, 1913.



more demand the services of men of special training. No definite data is at hand on the consumption of insecticides and fungicides but the statement may be ventured that the annual outlay for this class of agricultural material is fully as great and probably greater than that for fertilizers.

The most pressing need for study at present is in the origination and perfection of methods of examination of these substances which are upon the market in endless variety and are of such complex composition as to defy ordinary analytical methods. An intelligent study of analytical methods presupposes some slight knowledge, at least, of the nature and source of the raw materials and of manufacturing processes to know what impurities to look for and to fairly judge their permissible limit in commercial samples.

Some of the purely research problems that present themselves for solution are such questions as: How does sulfur really destroy insects and fungi? is it through oxidation of the sulfur or by actual volatilization of the sulfur as such? What types of lead arsenate are present in the commercial pastes? are they acid, neutral, or basic, or mixtures? What is the active principle in pyrethrum, quassia and hellebore?

The above and many other questions of greater or less importance have often been asked in vain. These are all problems to be solved largely by the chemist and naturally by one who has had some special training in this particular branch.

Occasionally, valuable articles have appeared in the chemical literature but the writer has often wondered that more attention has not been given to a subject of such great economic importance to the agricultural interests.

This paper is presented with the hope of arousing interest in the subject of insecticide chemistry and presenting a topic little known in chemical circles, that of insecticide legislation.

It is hoped that in time a sufficient number of the members of the Chemical Society may become engaged in this line of activity to organize a section composed of those interested in the chemistry of insecticides and fungicides.

Except those of you who have happened to cross the path of the insecticide inspectors in this state or the Federal inspectors, it is presumed that the majority are somewhat unfamiliar with the topic as announced. It is thought, therefore, that a brief historical sketch of this class of legislation would be of interest, before taking up the discussion of the California law in operation at the present time, as well as some of the events that led up to its passage.

#### POTATO BUGS AND PARIS GREEN

The commercial manufacture of insecticides in this country has been developed entirely since the year 1860, and is intimately associated with the advent of the potato bug in the middle western states. This insect was originally a native of the Rocky Mountains, feeding upon the native vegetation. The saying that "necessity is the mother of invention" is well corroborated by the experiences with this pest. The account of man's battle against this insect is so well given in Lodeman's "Spraying of Plants" that the writer cannot do better than to quote from him. "This insect, . . . , began to travel eastward when potato culture had extended so far west that the plant was grown in the territory occupied by the beetle. It then left the plants upon which it had been feeding, and attacked the potato vines. The march to the east then followed. In 1859, the insect had reached a point one hundred miles to the west of Omaha City, in Nebraska" (Riley). In 1868, it extended to central Missouri and southern Illinois. In July, 1870, the insect was found in Ontario, Canada; and in 1872, it arrived in central New York. Two years later, it reached the Atlantic coast, having crossed nearly two-thirds of the continent in the short space of fifteen years.

"The insects ate as vigorously as they traveled. Potato fields were stripped of every vestige of foliage; desolation could be seen everywhere; and as this increased, the yield of tubers decreased. At first it seemed that nothing could stop the ravages

of the pest, and it threatened the entire potato industry of the country. All known remedies failed, and the future must have appeared dark to the Western planters, until some remedy could be found that would destroy the beetles and save the foliage of the vines."

Fortunately, this remedy was soon found; but by whom is not a matter of history. In those days Paris green (copper aceto-arsenite) was the usual pigment for painting the window shutters and screen doors and some one found that this dry paint when dusted over the vines poisoned the insects to almost complete annihilation, with little or no injury to the plants. The news soon spread and new applications were found for its use in combating other insects. Dr. Cook, our own State Commissioner of Horticulture, was largely instrumental in having its use adopted as a remedy against the codling moth of the apple tree. He was then a Professor at the Michigan College of Agriculture. At any rate its use spread rapidly and the factories were severely taxed to meet this sudden and unexpected demand. New and more rapid methods of manufacture had to be developed to turn out tons of this material where formerly the demand had been comparatively small. In some cases the results were disastrous. Hasty manufacture sometimes resulted in a green that was deficient in arsenic. This difficulty was easily overcome by the ingenious mind of the chemist and the material was strengthened by the addition of white arsenic. The application had, by this time, come to be done almost entirely by means of spraying a suspension of the green in water. Paris green is itself quite insoluble in water but the white arsenic adulteration was sufficiently soluble to have a very serious effect upon the plants. Sodium arsenite which was used in its manufacture was not always completely washed out with a like disastrous result. Some thrifty manufacturers even sought to attain their dreams of wealth and a trip to Europe by the sale of some perfectly harmless and inefficient green powders. And so there came to be upon the market three classes of unsatisfactory Paris greens as follows: (1) bogus, (2) adulterated, and (3) low grade.

This state of affairs naturally led to the study of cause and effect. It soon became evident that some means of protection against unscrupulous and careless manufacturers must be found. Legislation was adopted as the remedy.

#### NEW YORK'S PARIS GREEN LAW

New York appears to have been the first state to enact legislation governing the sale of Paris green. In 1898, an Act was passed to prevent fraud in the sale of Paris green. This law required that manufacturers and dealers in Paris green submit to the Commissioner of Agriculture a statement setting forth: (1) The brands to be sold. The number of pounds contained in each package, together with the name and place of manufacture. (2) The amount of arsenic in the Paris green. This statement was to be considered a guarantee of each package sold and the minimum of arsenic trioxide was set at 50%. (To prevent the strengthening of low-grade greens with free arsenious acid an amendment was later passed, specifying that the arsenic must be in combination with copper and that the water-soluble arsenic should not exceed 3.5 per cent.)

#### OTHER EARLY LAWS

Oregon and Texas followed in 1899; California and Washington in 1901; and Louisiana at about the same time; New Jersey in 1906; Minnesota in 1909.

Oregon was the first state to pass laws to regulate other insecticides than Paris green. Their law included: "Paris green, arsenic, London purple, sulfur, or any spray material or compound for spraying purposes."

The Texas law sought to regulate "any commercial poison or any chemical or mixture used as a commercial poison, such as London purple, arsenic, Paris green, or any poison used for the purpose of destroying the boll worm or other pests."

The early Paris green laws were uniform in specifying a total



content of 50 per cent of arsenious oxid for Paris green. Low-grade greens were consequently strengthened by the addition of the necessary amount of free arsenious oxid to comply with the 50 per cent provision and passed inspection in many cases. As free arsenious oxid is very injurious to foliage, the results may be imagined. The entire abandonment of Paris green for spraying purposes was at one time considered on this account.

It is believed that the California Agricultural Experiment Station (through the publication of *Bulletin 126* by Profs. Woodworth and Colby) was the first to call attention to this condition and to advise the restriction, by legislation, of the amount of water-soluble arsenic in Paris green.

#### SOLUBLE ARSENIC LIMITED

The California law was very similar in operation to New York's law, but two steps in advance were taken: (1) It was specified that the arsenic must be in combination to the extent of 50 per cent, and (2) that the water-soluble arsenic must not exceed 4 per cent. Washington and California may claim almost equal honors in the actual passing of laws restricting the amount of water-soluble arsenic in Paris green, with Washington two days in the lead. The Washington law was signed by the Governor, Feb. 26, 1901, while that of California became a law by constitutional limitation two days later in the same year.

#### APPEARANCE OF OTHER INSECTICIDES

The laws previous to 1901 had, as their principal concern, the regulation of the sale of Paris green, as this substance was the first to be made commercially. Other more reliable and efficient arsenical poisons began to appear and be recommended, notably, lead arsenate and London purple. The efficiency of these sprays soon led to the use of many other preparations of a widely different character. Chemical investigation of these other substances in this and other states clearly showed the need of standardizing insecticides and fungicides of whatever nature.

#### THE FEDERAL LAW

Responding to this clearly shown need, the Federal Government passed what is known as the Insecticide Act of 1910. This law is quite comprehensive and is intended to regulate the traffic in a large class of materials, many of which were heretofore not covered by any laws—insecticides and fungicides. To be sure that the law would be inclusive, the term "Insecticides" is defined in the law as follows: "any substance or mixture of substances intended to be used for preventing, destroying, repelling, or mitigating any insects which may infest vegetation, man or other animals, or households, or be present in any environment whatsoever." The word "Fungicide" is defined in equally comprehensive language. Standards are also fixed for Paris green and lead arsenate.

#### MORE RECENT STATE LAWS

Subsequent to the passage of the Federal Insecticide Law, Maine, California, Ohio, North Dakota, Michigan, and New York passed new laws or amended their old laws to regulate the manufacture and sale of all insecticides and fungicides, the latter terms being defined in the laws in practically the same language as that used in the Federal Law. Minnesota's law of 1906 was also of the same nature. Some of the laws were even more stringent than the Federal Law in the matter of requiring the nature of the contents of packages to be fully declared upon the label.<sup>1</sup>

#### CALIFORNIA'S PRESENT LAW BEFORE AMENDMENT

ORIGIN—Seeing the need of more adequate and comprehensive regulation of insecticides other than Paris green (whose use had largely been replaced by other materials) as shown by the investigations of Colby, Prof. Woodworth, Entomologist of the California Station, brought the matter to the attention of the California horticulturists, and published a bulletin in 1906, calling attention to the need of a more comprehensive law.<sup>2</sup>

<sup>1</sup> Since going to press it has been learned that Montana has passed an insecticide law and that New Jersey has amended her law to include all insecticides and fungicides.

<sup>2</sup> Cal. Agr. Exp. Sta., *Bull.* 182.

The subject was brought up at a session of the (Cal.) State Fruit Growers' Convention and a committee was appointed composed of users and manufacturers of insecticides. The present law is the result of the efforts of this committee. The bill as originally proposed was based upon the state fertilizer law which had been in successful operation a number of years at the time. In fact, it was the same bill with only the necessary verbal changes to make it applicable to insecticides. The draft of the bill as finally presented to the Legislature for enactment, contained the essential features of the original with some additions to make it correspond more closely to the Federal law and a change in the proposed manner of financial support of the measure.

It is not the intention, in this paper, to take up in detail all the features of the law but only those which will be discussed which are thought to be the more important or that are distinctive in some way.

ADMINISTRATION—The insecticide law now in operation in California (California Statutes of 1911, Chapter 653) went into effect July 1, 1911, after having been signed by the Governor at the previous session of the Legislature. By the terms of the Act the administration was placed in the hands of the Director of the Agricultural Experiment Station in person or by deputy. Prof. Wickson, the Director at that time, designated the head of the Entomological Division to be in immediate charge of the work, which arrangement was made by the Regents of the University. The chemical work was delegated to Prof. Colby and the writer.

REGISTRATION—The law required the annual registration with the Secretary of the Board of Regents of the University, of all manufacturers, importers and dealers in insecticides and fungicides, stating the component parts of the substances which they proposed to offer for sale. This requirement was made so that the office might more easily and accurately keep informed of the materials being offered for sale in the state.

LABELING—Proper labeling of each package was also required, stating:

- (1) Name, brand or trade mark, if there be any.
- (2) Name and address of the manufacturer.
- (3) Place of manufacture.
- (4) Chemical analysis, showing:
  - (a) The percentage of each substance claimed to have insecticidal value.
  - (b) The form in which each is present and the materials from which derived.
  - (c) The percentage of inert ingredients.

The object of this provision was to enable the user to know the insecticidal value of the material, and also to make the manufacturer more careful as to the composition of his products.

This section was the most radical of any of the requirements and was the one most seriously objected to by those who wished to oppose the law. Most manufacturers accepted the section as a good one and complied with it after they saw the advantage to be gained in protection from inferior goods sold and guaranteed to be equal in value to the better grades. Practically the only serious objections came from the makers of "secret" remedies who had been profiting by the use of fictitious names.

PROPRIETARY INSECTICIDES AND FUNGICIDES—Many valuable and reliable remedies are on the market under patented names or brands which do not convey to the user any idea of their composition. Many of these are sold at their true worth with the name or trade mark used only as an identification mark to designate the certain characteristics or quality or worth of the particular preparation. The following remarks and illustrations are not intended to be in any way personal or to be aimed at any particular substance that has come to the attention of the office.

The few manufacturers that strenuously objected to publishing

their formulas argued that it was wholly without justice to require the publication of a secret formula upon which years of study and experimenting or perhaps many dollars had been spent in its perfection. They pleaded that their business would be ruined, that other manufacturers would be in possession of their formulas and the market would be flooded with similar preparations, if the secret of their wonderful and mysterious compounds were known. Such objections would indeed be valid if they were always based upon fact. So far as can be ascertained by study of the literature and examination of the formulas of the remedies that have been registered in the office, there have been very few actual "discoveries" of new insecticides which are not very simple compounds already known and made public. The most noteworthy "discoveries" and "secrets" in this class of goods are not the discovery of the insecticide itself but the discovery of some efficient and cheap coloring matter, or some powerful and pleasant smelling perfume to mask the presence of some very common remedy. The mysterious and wonderful properties ascribed to them are too often found on the outside of the package, composed of printer's ink, rather than upon the inside of the package. Among illustrations of this kind may be mentioned the coloring of borax with iron rust; the sweetening of the odor of kerosene with oil of citronella; the coloring of carbon disulfide with iodine and masking its telltale odor with oil of mirbane.

It is true that the pleasing color and pleasant odor of an insecticide has some aesthetic value, but this would scarcely warrant a selling price for pink kerosene many times more than the Standard Oil Co. would care to charge.

While this way of purchasing insecticides is tolerated by the public through long usage, the same procedure would not be tolerated, for a moment in the buying of nursery stock for instance. A nurseryman who had developed a new kind of fruit would scarcely hope to sell his trees by telling the prospective purchaser that the trees were of exceptionally fine variety and were guaranteed to produce good fruit but that he preferred not to tell what kind of fruit trees they were as it was a great secret developed by the originator.

**PENALTIES AND DEFINITIONS**—Other sections provide penalties for infractions of the law and specify what constitutes misbranding and mislabeling, and other necessary legal verbiage.

**THE WORK OF THE OFFICE**—The annual sampling and analysis by the Director or his deputies of all registered substances was also required. As the registrations began to come in, and the list of registered materials began to grow, it very soon became evident that the literal fulfillment of this requirement would be a physical impossibility. The number of registered brands for the first two years of the operation of the law was well toward 10,000. The purpose of this section was, however, fulfilled by the collection of a representative number of samples of each class of goods and the inspection of the stock and labels of dealers to see that they were at least prepared to comply with the section on labeling.

Quoting from the annual report of the Director<sup>1</sup> during the fiscal year ending June 30, 1913, this work was performed by "seven inspectors, who traveled by rail, stage and boat, approximately 9672 miles, visited 332 towns, and rendered detailed reports on the insecticides stocked by 1631 dealers of whom 984 were operating under licenses issued by the University, the balance handling only registered goods in original packages. The number of brands registered and labels inspected was 9646, the number of samples taken up was 777 and of analyses made was 553."

**THE WORK OF THE ANALYTICAL LABORATORY**—During the first year the chemical work was performed by two chemists who devoted only a part of their time to the work and one who devoted his whole time to the work with the exception of two months'

inspection during July and August. The analytical force was strengthened the second year by the appointment of Mr. M. R. Miller to devote his whole time to analytical work except two months of inspection in the summer.

A large amount of time was necessarily consumed in the equipment of adequate laboratories, the systematizing of the work, study and classification of the multitudinous preparations on the market, and perfection and development of methods of examination.

The publication of the results of analysis has been somewhat neglected, due to the pressure of this other work. It is felt, however, that much good may be accomplished by the frequent publication of the results of examination, comparing the different materials on the market. This work will receive more attention in the future.

#### AMENDMENTS TO THE LAW

At the time that the law was proposed, a bulletin was issued as already noted, giving the text of the bill and "comments, suggestions, and expressions of opinion of all parties interested in the measure" were solicited.<sup>1</sup> About four years elapsed between its proposal and its presentation to the legislature in 1910 and in the meantime no serious opposition was manifested to its passage.

**OPPOSITION MOSTLY FROM THE DEALERS**—Very little hostility to the law was openly expressed by the manufacturers, although as mentioned before, some of the promoters of insecticides of "common" origin but "aristocratic" price objected to the printing of their formulas.

Retail dealers in many instances considered it a hardship to be obliged to pay the annual registration fee of one dollar and the necessary notary fee for the affidavit. The office in charge of the administration of the law expressed a willingness to support an amendment doing away with the registration system, provided that the income for the support of the law be made up in other ways.

Originally the Director was authorized to *take* a sample not exceeding two pounds in weight from any stock of insecticide or fungicide. The taking of samples without remuneration was clearly an injustice in principle, but in most cases the samples were given cheerfully. In this case also the office in charge had expressed itself as unopposed to an amendment providing for the purchase of samples if sufficient funds were provided for the purpose.

The wording of the law being largely based upon a law written for the control of an entirely different class of merchandise, it was to be expected that there would be some defects, but these were not considered of a sufficiently serious nature to be changed without further trial.

Certain dealers, it seems, still desired to consider themselves "persecuted" even though the office had agreed to support measures that they desired. As a result of their *silent* activity in the last Legislature, amendments were passed changing the law quite materially. The parentage of the amendments and the true spirit of the opposition to adequate insecticide legislation in the state, appears to be well expressed in a prominent drug journal of the state,<sup>2</sup> under the heading of "Join the California Pharmaceutical Association" and reading as follows: "Through the efforts of this association, you will no longer be persecuted through the former obnoxious insecticide laws."

**REGISTRATION SYSTEM ABOLISHED—SAMPLES TO BE PURCHASED**—The amendments do away with the entire registration system and authorize the *purchase* of samples instead of the *taking* of them as in the old law. The attitude of the office has already been expressed on these two points.

**LABELING—A STEP BACKWARD**—The labeling of packages, giving the percentage amounts of the active constituents, is no

<sup>1</sup> Annual Report of the Director, Cal. Agr. Exp. Sta. from July 1, 1912, to June 30, 1913.

<sup>2</sup> Cal. Agr. Exp. Sta., *Bull.* 182.

<sup>3</sup> *Pharmacraft*, Oct., 1913, p. 5.

longer required, although a "general" statement of the nature of the contents must be given. This seems to be the most essentially backward step taken and again permits the fanciful name to possibly determine the selling price of an insecticide, rather than its true value.

**TIME OF TAKING SAMPLES CHANGED—AN IMPROVEMENT**—The part of the section specifying the time of taking of samples has been omitted. This appears to be one of the good features of the change, as the time of taking of samples was previously within a period of two months annually, which afforded an opportunity for an annual clean-up of doubtful material on hand for those who might happen to be so inclined.

**NO VARIATION NOW ALLOWED**—Another part of this same section was left out, which allowed a 5 per cent variation from the professed standard without being considered a case of misbranding. For high percentages, this was undoubtedly too great an allowance. For instance in the case of bluestone, if the article were guaranteed to contain 100 per cent copper sulfate and analysis showed it to contain only 95 per cent, it could not be considered to be mislabeled in the language of the law. This lower grade article could successfully compete with bluestones of grades up to 100 per cent, in so far as labeling was concerned. On the other hand, the 5 per cent variation seems reasonable for the low percentages.

**METHODS OF ANALYSIS NOT SPECIFIED**—Specification of the methods of analysis was omitted in the amended law and the way is thus left open for argument and dispute where there is a difference of opinion as to the proper procedure, or a variation in results by different methods.

**EXEMPTION OF CERTAIN PREPARATIONS**—Drugs and chemicals listed in the U. S. Pharmacopoeia and National Formulary and medicinal and toilet preparations guaranteed under the Food and Drug laws are exempted from the supervision of the law. This seems quite proper and reasonable as they are already under the control of the Food and Drug Officials.

The above changes were all accomplished by the passage of Assembly Bill No. 623 which was referred to the Committee on Medical and Dental Laws.

#### ANOTHER AMENDMENT

Still another bill was passed to further mutilate the law. Senate Bill No. 670 stands as mute evidence of superfluous effort by its promoters. This was referred to the Committee on Agriculture, was approved, passed by both houses and signed by the Governor. This bill, as passed, added a new section to the law as follows; "The following insecticides and fungicides or materials to be used for insecticidal or fungicidal purposes may be sold by grocers and dealers generally without restriction and without the registration fee, permit or license being required of them, *viz.*: insect powders, poison fly paper, sticky fly paper, borax, moth balls, gum camphor, spirits of camphor, blue ointment, oil of eucalyptus, castor oil, ant poison, sheep dip, lice killer, sulfur, bluestone."

This was clearly an attempt to create a favored class of dealers who did not care for various reasons to be bothered by the inspectors and the annual registration. The list of substances which it was sought to have placed in the immune class includes some articles already supervised by the Food and Drug Laws; others have been found to be free of adulteration. Still others have been found to be subject to grave misrepresentation, particularly the lice killers and the sheep dips. The other bill previously referred to abolished the whole system of registration so that the grocers need not have been specially mentioned, nor the articles that they wished to sell without registration.

#### ATTITUDE OF THE OFFICE

The situation concerning the amendments to the law is summed up by the entomologist in charge as follows: "While apparently removing some of the safeguards, the present law may still sufficiently protect the user. It will be the special task of the Insecticide Laboratory during the next two years to determine whether the users' interests are sufficiently protected and if not the law can be further amended."

The office sincerely desires to cooperate with all manufacturers and dealers who are making an honest effort to provide the consumers of the state with materials of worth and reliability, in any effort to secure the passage of legislation which will be fair both to seller and buyer.

In order to more fully understand the situation, the entomologist has many times met organizations representing both parties in interest, has had many conversations, written many letters, and has always shown a desire to adequately protect the interests of both parties. The chemist in charge of the analytical laboratory has visited many factories in the state and corresponded with many manufacturers outside of the state, in an effort to study methods of manufacture, feeling that more intelligent work could be done in the examination of the samples that come in for inspection.

#### PUBLICATION VS. PROSECUTION

As expressed by Prof. Woodworth in the first paragraph of his instructions to inspectors: "The purpose of this office is to prevent rather than to detect fraudulent practices in the sale of insecticides and fungicides." and the policy thus expressed has always been adhered to. This is indicated by the fact that no prosecutions have as yet been made, although many cases of misbranding and mislabeling have come to the attention of the office. Dealers and manufacturers in general have shown a desire to correct violations of the law when their attention has been called to the facts.

It is thought that more good can be accomplished by publicity of facts than through prosecution, which latter is useful only as a last resort against those who persistently and purposely violate the law.

INSECTICIDE LABORATORY  
UNIVERSITY OF CALIFORNIA, BERKELEY

## CURRENT INDUSTRIAL NEWS

By M. L. HAMLIN

### CORRECTION

The references in this department of THIS JOURNAL, 6 (1914), 429-430, to the *Journal of Gas Lighting and Water Supply* should have read Volume 125 instead of Volume 97 as printed.

### MEASURING RAPIDLY CHANGING TEMPERATURES

A method for measuring temperatures as high and as rapidly changing as those in the cylinder of an internal combustion engine has been partially worked out and tested by A. Petersen, who describes his experiments in the *Zeitschrift des Vereines deutscher Ingenieure*, 58 (1914), 602.

Two forms of apparatus were tried—a thermocouple and a resistance pyrometer. These had to satisfy the following conditions: (1) The mass of the element must be negligible compared with that of surrounding bodies. (2) The element must have the highest possible melting point. (3) The instrument for measuring the electric current must have the least possible drag. (4) The recording device must exert no retarding effect on the measuring instrument.

For the resistance pyrometer a wire 0.02 mm. in diameter of an alloy containing 65 per cent platinum and 35 per cent iridium was used; this withstood a temperature of 1850° C.



The thermocouple consisted of a wire of pure platinum and one of an alloy of 90 per cent platinum and 10 per cent rhodium; this withstood  $1650^{\circ}\text{C}$ . The lead wires were in every case of the same material as the wires of the element to which they were fused, and were, in the final experiments with an engine, mounted in suitable insulating material passing through the cylinder head.

For the measurement of the current an Einthoven string galvanometer was used and its deflections were recorded photographically on a constantly moving roll of sensitized paper.

The thermocouple and resistance pyrometer were standardized by heating in an electric furnace of platinum whose temperature could be measured, and the galvanometer was adjusted to constant readings each time it was used, by means of a known and constant current.

Since the instruments were to be used in a four-cycle gasoline engine making about 600 r. p. m., the fine wires must be able to attain and lose a temperature of  $1800^{\circ}$  in 0.1 second. This was tested by passing the wires, fastened to the rim of a disc revolving at a known rate, through Bunsen flames and observing the resultant curves in the recording device. The dimensions described above gave satisfactory results.

The series of experiments actually made in an engine cylinder was merely of a preliminary nature, more for the purpose of studying the instruments than the engine; the results prove the practicability of the method for investigating thermal changes under these and similar conditions.

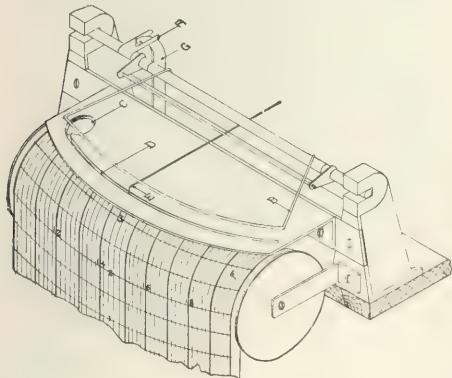
#### THE AUSTRALIAN COAL TRADE

The Australian coal trade for the quarter ended March 31st last shows a big increase in exports, especially to foreign countries, *Engineering* (London), 97 (1914), 714. The exports were 1,365,000 tons, as compared with 1,047,000 tons for the first quarter of 1913. Of these totals there were just under 600,000 tons exported to foreign countries, as compared with 344,000 tons in the March quarter of last year. The biggest increase is in the Far East, a quarter in which Australian trade all round has in recent years made strong advances.

#### A NEW RECORDING DEVICE

A recording device for pyrometers and similar instruments, designed on novel lines, has recently been put on the market. It is illustrated in the accompanying cut.

When free, the needle, which carries a fine wire, E, bent downward,



swings above a V-shaped slot, D, in the sheet of metal mounted horizontally above the drum. This slot is supplied with ink from well C, and the slot tapering slightly throughout its length, the ink flows freely to the extreme end. The lever G is

periodically lifted by a cam, driven by a clock, mounted in the lower part of the recorder case, allowing depressor B to press down upon the needle until the point passes through the film of ink, carrying enough ink to make a dot upon the chart. No more ink than needed to make the dot, or dash, if a multiple record, is deposited upon the chart. By holding the needle against the chart, a dash of any desired length may be made, depending upon the time of depression of the needle.

From one to five galvanometers, mounted side by side in the recorder case, may use this type of inker, giving simultaneous records at any desired interval.

#### THE KONGSBERG SILVER WORKS, NORWAY

*Engineering* (London), 97 (1914), 566 reports that the venerable Kongsberg silver works in Norway, which boasts a history extending over some three hundred years, has lately been modernized in almost every respect. The old smelting methods for the poorer ore, whereby much silver was lost, have been abandoned, electric power has superseded water power, and locomotives have displaced horses in the mines which are situated at two levels. The lower mines were not worked for the greater part of the last century, but prospects there are now very favorable, and this part of the mines is expected to yield at least 5000 kg. of silver annually for the next ten years. The upper-level mines have been worked with varying results, the King's mine having been the mainstay for the last century; it is now 3000 ft. deep, of which 1220 ft. are below the level of the sea. After a disappointing section towards the bottom, some rich ore has now been found. The output of silver has been increased of late years, and during the financial year 1911-12 it amounted to 23,060 lbs., a figure which is likely to be materially exceeded, with the aid of good new findings and the improved plant.

#### PRODUCTION OF ZINC IN EUROPE, 1913

According to *Engineering* (London), 97 (1914), 611 the production of zinc in Europe last year amounted to 671,160 tons, showing an increase of 20,490 tons, as compared with the output for 1912. Production fell off last year 2455 tons in Belgium, 1120 tons in France and Spain, and 1135 tons in Poland; but it increased 1015 tons in Silesia, 10,845 tons in Rhenish Prussia, 1885 tons in Great Britain, 385 tons in Holland, 2070 tons in Austria and Italy, and 9000 tons in Norway. The production of zinc throughout the world last year was estimated at 990,065 tons.

#### MINING IN CHINA

The British Consul at Changsha is quoted in *Engineering* (London), 97 (1914), 534, to the effect that mining is the most flourishing industry in Hunan, since not much capital is required to exploit superficially the rich deposits of that province, and that the new mines started in 1912 include silver, antimony, iron, lead, coal, manganese, cinnabar, tin, sulfur, copper, copperas, gold, zinc, and salt. Prospecting activity is also reported in the Fukien province for tin and iron, and in Kwantung for gold, tin and coal. The most important coal mines in China are those worked by a British company at Kaiping, in Chihli—that is, by the Chinese Engineering and Mining Company, and by what was a rival Chinese company working the neighboring mines at Lanchow. The competition between these two companies is now removed by a working agreement, and this is expected to assist greatly the development of the resources of the whole coal basin affected. The combined output of the two collieries in 1912 was 1,706,658 tons. The Pekin Syndicate mines in Hunan produced 549,877 tons in 1912, against 417,190 tons in 1911. The Hungshang and Fangtze mines in Shantung turned out 573,696 tons, as compared with 486,553 tons in 1911. No figures are at hand for the important

coal mines at Fushan, near Darien, but the present output is said to amount to 5000 tons daily. In order to encourage the mining industry, the Minister of Commerce and Industry, Mr. Chang Chien, is at present devoting attention to the framing of regulations, which if adopted, will place the mining industry of China upon a proper basis, and permit of development with foreign capital, knowledge, and experience. The four chief points which require remodelling, and which are receiving attention, deal (a) with the ownership of the mining property, (b) the extent of mining areas, (c) the tax to the Government, and (d) foreign participation. Mr. Chang Chien proposes that foreign and Chinese capital shall have equal rights. He expresses the idea (which he hopes to have embodied in law) that foreigners should be entitled to buy whatever shares they like on the Stock Exchange, and it is his intention to establish stock exchanges under Government regulations, which will be open to foreigners, and which will be the medium whereby foreigners may obtain scrip in mining ventures, as and when they please. The control of mining properties will be entirely in the hands of those who secure the mining rights. With a view to classifying the minerals of China and the areas in which they abound, a Mining Bureau will be established, whose business it will be to attend to this work and to carry on a continuous policy of development on behalf of the Government. Already a beginning has been made of a survey of the mineral deposits of Shansi province, and a similar work will be carried out eventually with regard to each province. The results will be compiled for public use, and it will be the aim of the Bureau to assist the investing public to develop properly the rich resources that are now practically untouched.

### THE OIL RESOURCES OF THE BRITISH EMPIRE

In a recent lecture before the Society of Arts, London, Dr. F. W. Perkin discussed the oil resources of the British Empire, *Engineering* (London), **97** (1914), 459. In Great Britain itself only traces of mineral oil have been located. The occurrence of natural oil in Derbyshire suggested to James Young that the oil, which soon gave out, had been produced by the terrestrial heat from shales, and he had, in 1850, taken out the first patent on a distillation process of shale oil. Shales now yield from 16 to 40 gallons of oil per ton, the average being 23 gallons, and the oil-shale mined in Scotland rose from 2,690,028 tons in 1907 to 3,116,800 tons in 1911.

Canadian natural oil has for some time had a bad reputation, owing to its sulfur content and bad smell, and when that trouble was overcome, the production began to decline; the number of barrels of oil produced fell from 788,872 in 1907 to 243,614 in 1912. Recently more oil has been found in Alberta, on the slopes of the Rocky Mountains, and Canada promises to become a rich oil field. In New Brunswick 140 men, in December, 1913, were employed in shale-oil works, and natural gas is used on the Intercolonial Railway for car-lighting and other purposes. Australia is not at all rich in oil, but plenty of oil shale occurs, chiefly in New South Wales, where the term "kerosene" is rather inaptly applied to a variety of torbanite, a cannell or bog-head mineral; the production of oil shale in New South Wales rose from 47,331 tons in 1907 to 75,000 tons in 1912. Oil shale is also found in Queensland, in Southern Australia, and Tasmania, but the oil finds are not important. The Taranaki oil wells in New Zealand produce 6720 gallons per week. Papua is promising as to oil. The largest sources of oil in India occur in Burma, and the yield of the various oil wells there rose from 173,400,000 gallons in 1908 to 245,300,000 gallons in 1912. Assam has since 1908 given over 3,300,000 gallons every year, the yield increasing to 3,747,360 gallons in 1912. Trinidad is, of course, famous for its asphalt lake, but recently oil-boring has likewise been very successful, and 250,000 barrels were exported in the one year 1911-12.

In Africa oil has so far not been mined in large quantities. Compared to other countries, the oil production of the British Empire is still small. The total production is at present estimated at 1,359,000 tons, of which India contributes about one million tons. That aggregate represents 2.06 per cent of the total oil production of the world, to which the United States contributes 63.63 per cent; Russia, 18.2; Mexico, 5.9; Roumania, 3.72; the Dutch Indies, 3.02; and Galicia (Austria), 2.14 per cent.

Having thus surveyed the mineral oil wealth, Dr. Perkin turned to the coal-tar oils, peat-oil, vegetable oils and fish oils. The vegetable oils, he said, are utilized in the manufacture of varnishes, soap, and food-stuffs, like margarine; that they have not answered as lubricants has been due partly to the defective methods of refining.

### COAL STORAGE AND GAS MANUFACTURE

In 1910 the Düsseldorf Gas Works took quantities of coal, consisting of 150 tons each, from a colliery of the Westphalian Coal Syndicate, and stored one part in the open in a heap 11 ft. 6 in high, while the other 150 tons were piled nearly 10 feet high in a shed, with normal storage conditions prevailing as far as possible in other respects. In July and August last year—i. e., 3½ years later—10 tons of each of these separately stored coals were sent to the Experimental Institute of the German Association at Karlsruhe, and distilled separately for purposes of comparison, special care being taken that similar conditions prevailed in each case. Dr. Karl Bunte communicated the results of these interesting experiments in a recent number of the *Journal für Gasbeleuchtung*, and the following table is reprinted in the *Jour. of Gas Lighting and Water Sup.*, **126** (1914), 494.

COMPOSITION OF COAL (PERCENTAGES)	STORED IN SHED		STORED IN THE OPEN	
Ash.....	10.61		11.11	
Moisture (Total).....	0.21		5.46	
Up to 110° C.....	2.26		1.34	
Pure carbon substance.....	86.92		82.09	
CARBONIZING RESULTS				
Oven temperature.....	1185° C.		1180° C.	
Gas production (N.T.P.).....	33.9 cubic meters		33.9 cubic meters	
Coke.....	71.9 kg.		71.9 kg.	
Tar.....	3.8 kg.		4.4 kg.	
Crude liquor.....	6.9 kg.		8.4 kg.	
Gross calorific value.....	5275 calories		5250 calories	
NH <sub>3</sub> per 100 kg. of coal.....	275.7 grams		269.0 grams	
COKE				
Quite fine dust.....	19 per cent		32 per cent	
After a fall of 11 feet.....				
Size—Over 45 mm.....	48 per cent		34.5 per cent	
Size—Over 30 mm.....	25.7 per cent		22.9 per cent	
Size—Over 5 mm.....	19.3 per cent		31.3 per cent	
Size—Under 5 mm.....	7.0 per cent		11.3 per cent	

While no general conclusions as to the effect of storage on coal can be arrived at from these tests, it is interesting to note that, at any rate in the case of this particular coal, there is no material change in the gas production and the calorific value of the gas produced. However, the coke obtained from the open-stored coal is considerably inferior to that from the other. The results are practically equal all through, except in the case of the gas liquor, which is explained by the difference in moisture content of the two coals.

Further experiments are being made, with the help of another large gas works, on the effect on coal of storage, especially with a view to comparing stored with freshly mined coal. The results of these researches will be published at a later date.

### THE CORROSION OF IRON BY DISSOLVED OXYGEN

The question of the corrosion of iron water pipes by dissolved oxygen has been studied experimentally by J. V. Cobb and G. Dougill, *Jour. Soc. Chem. Ind.*, **33** (1914), 403.

Such an investigation seemed to be necessary, because several cases of such rusting had come to the notice of one of the authors, when the water was satisfactory according to the ordinary chemical tests, and there was no reason to suspect abnormality in the iron. The authors' conclusions are as follows: (1) That in our experiments a very large proportion of the dissolved oxygen in the water supply used for a simple heating system consisting

of one pipe was not present in the water or gas leaving, but had been absorbed in the pipe. It was presumably used up in rusting the iron, and a large quantity of rust was actually formed. (2) That about half the loss of oxygen occurred in the first foot length of the pipe—the heater. (3) That the further loss of oxygen occurred in the 5 feet of pipe beyond the heated length, and could be prevented if the expelled gases were mechanically taken off at the end of the heated length. (4) That in small-scale experiments with pure iron foil the expulsion of dissolved gas from the water by previous boiling was an effective means of preventing rusting. (5) That in similar small-scale experiments it appeared that the rusting of iron foil could be almost prevented by treating the cold air-saturated water with the sodium hydroxide and ferrous sulfate necessary to take up the oxygen dissolved in the water supply.

### THE LIGHTING OF RIO DE JANEIRO

Rio de Janeiro is said by the *Jour. Gas Lighting and Water Sup.*, 126 (1914), 492, to be one of the most lavishly illuminated cities in the world. In 1912 over \$1,500,000 were spent on public illumination both by gas and electricity, 7,918,660 cubic meters (279,655,400 cubic feet) of the former and 11,819,352,017 kilowatt hours of the latter being consumed. For private illumination in the same year 16,291,915 cubic meters (575,365,270 cubic feet) of gas and 11,653,036 kilowatt hours of the electric current were consumed.

### THE UTILIZATION OF SULFITE-CELLULOSE WASTE

The question of handling the waste liquors from sulfite-cellulose factories may involve not only the possibility of their commercial utilization, but the very existence of the factories themselves. Professor Lassar-Cohn discusses both sides of the problem in an article in *Chemiker-Zeitung*, 38 (1914), 657, and gives the solutions arrived at in the case of two factories in Königsberg, Prussia, which had been closed by the police for polluting the Pregel River. In one case the factory waste was turned into irrigating ditches and in the other into the Frischer Haff. Contrary to the fears of the local population, it did no harm in either case, but rather, in Lassar-Cohn's opinion, acted as an excellent fertilizer in the ditches, and in the Frischer Haff (in which, of course, its dilution was enormous) actually aided the fisheries which increased \$100,000 from 1912 to 1913.

While this disposal of the waste was satisfactory in that it assured the existence of the factories, it brought them no return. The enormous quantities of waste liquors produced in the manufacture of paper by the sulfite process (2000 tons of dissolved substance are produced daily in Germany alone) make the problem of finding a commercial use for them an extremely tempting one, and the prize of 100,000 marks (\$25,000) offered by the Verein der Zellstoff und Papier Chemiker for a solution will be negligible compared with the returns which a successful patented process would bring in.

Because of the dilution of the liquors (10 per cent to 11 per cent solid substance), recovery by evaporation is expensive, and even when the residue has been recovered for use in briquetting, it has proved too deliquescent to be practicable. The author is of the opinion that the most promising method would be the precipitation in some way of the soluble resins and the recovery of tannin products, perhaps by condensation with a sugar or similar substance.

### CANADIAN COKE OVENS

The figures issued for 1913 by the Canadian Department of Mines show a coke production from coke ovens of 1,517,133 tons, as against 1,406,028 tons in 1912, *Jour. Gas Lighting and Water Sup.*, 126 (1914), 406. Over 68,000 tons of coke were exported last year, and nearly 724,000 tons imported. There were also produced 10,608 tons of sulfate of ammonia, 8,371,600 gallons of tar, and 3353 million cubic feet of gas. When the report closed, there were 1720 ovens in operation, and 1325 ovens standing.

### GERMAN AND ENGLISH EXPORTS OF AMMONIUM SULFATE IN 1912 AND 1913

German trade in ammonium sulfate for 1912 and 1913 is compared with that of England and the following table of exports published in *Chemiker-Zeitung*, 38 (1914), 593. In both countries the production increased in 1913 and the price fell; the German production will be still larger this year because of the manufacture of ammonia from atmospheric nitrogen by the Badischer Anilin- und Soda-Fabrik, estimated at 30,000 tons annually, but which can be increased in accordance with the demand.

GERMANY TO		EXPORTS (METRIC TONS)		GREAT BRITAIN TO	
		1912	1913		
Belgium	19,728	15,774	Germany	1,815	9,246
Denmark	92	45	Holland	2,178	
France	4,313	7,428	Belgium	31	5,090
Italy	3,816	8,550	France	7,550	8,825
Holland	19,121	18,195	Spain and Portugal	63,300	55,000
Switzerland	1,447	1,337	Italy	13,320	5,730
Spain	855	2,350	Japan	85,300	112,900
Ceylon	43	818	United States	38,650	36,470
Hawaii		2,441	Java	32,990	37,436
Japan	5,620	10,023	Other countries	40,000	
United States	902	5,629			
Brazil	965	428			

### DESTRUCTION OF AN ARTIFICIAL LEATHER FACTORY

On Friday morning, May 15th, shortly before 10 o'clock, the plant of the Mexican Crude Rubber Co., located at Solvay and Mackie Sts., Detroit, Mich., was almost totally destroyed by a series of explosions, accompanied by a swift fire. Of the twenty-seven chemists and operators in the plant at the time, nine were killed instantly, one died later, and six were more or less severely injured.

The building [described in connection with the accident, in *Engineering News*, 71 (1914), 1154] in which the explosion took place, was fairly isolated from adjacent buildings and was 50 × 200 ft. in plan, one story high, with no basement. Structurally, it was a steel frame with curtain walls and floor of cement mortar on ribbed metal lath. Heavy 8-in. H-sections formed the wall columns. The curtain walls 3 in. thick were carried to a height of 5 ft. above the floor level; above this, glazed metal window sashes were used to within about 2 ft. of the eave line.

In the rear of the building were storage rooms, a laboratory, cotton picker, presses, etc. A transverse partition wall separated this room from the central section of the factory in which the finished material was produced. In this finishing room were coaters, rollers, etc. The supply stores of the explosive chemicals and of raw cotton, used in the manufacture of artificial leather, were kept in a small separate brick building about 30 ft. to the rear of the main buildings, and were brought in as required.

The force of the explosion cleaned out practically every wall panel in the rear 125 ft. and the entire middle section of the roof down to the transverse partition. In some places the curtain walls were simply blown over onto the ground, while in others, the curtain wall sections were hurled 30 ft. away from the building; the central transverse partition was blown towards the front. The position of this partition and the presence of a hole about 3 ft. in diameter and 6 in. deep, ground into the concrete floor of the rear room indicate that one of the principal explosions occurred at this point. A large heavy milk can full of collodion cotton is known to have stood here and pieces of sheet metal were driven into adjacent timbers.

The steel frame seems to have suffered little damage; some of the exterior H-columns are buckled a little. The heat from the fire in the forward section of the building was probably intense, for horizontal angles in the rear partition of what was the office were bent and twisted.

Since the explosion killed outright everyone in the immediate vicinity, it will probably never be known definitely what its origin was, but it may well have been caused by the ignition of inflammable vapors by sparks from motor brushes.



# AMERICAN INSTITUTE OF CHEMICAL ENGINEERS

The Sixth Semi-annual Meeting of the Institute was held in Troy, New York, June 17th to 20th, 1914, with headquarters at the Rensselaer Hotel. The local arrangements were in the hands of Professor Wm. P. Mason, of Rensselaer Polytechnic Institute.

The opening session was held at 9.30 Wednesday morning in the Pittsburg Building of the Rensselaer Polytechnic Institute, where the members were warmly welcomed by Mayor C. F. Burns on behalf of the city of Troy, and by President Ricketts, of the Polytechnic Institute. President Ricketts spoke of the new course in Chemical Engineering recently established there in recognition of the rapidly growing importance of this profession, and extended a most cordial invitation to the visitors to be the guests of the Polytechnic at luncheon.

At the business session which followed, the reports of the Secretary and the Treasurer were presented and the standing committees reported: Chemical Engineering Education, Prof. J. R. Withrow, *Chairman*; Patents, Dr. L. H. Baekeland, *Chairman*; Standard Catalogue, Wm. M. Grosvenor, *Chairman*; Meetings, A. W. Ayer, *Chairman*. The business session was followed by a most interesting and comprehensive series of papers, short abstracts of which are given below.

## SOCIAL FEATURES

The Institute banquet was held at the Troy Club. Prof. Mason presided as toastmaster and introduced the first speaker, Dr. Charles Ferris, Medical Director of the New York State Reservation Commission, who gave a very interesting and instructive talk on the work and plans of the Commission at Saratoga. Prof. A. M. Green, Head of the Department of Mechanical Engineering at Rensselaer, told of the work at the Institute and outlined the intensive method of instruction adopted there. President Whitaker spoke for the Institute of Chemical Engineers. He summarized the work of the year and outlined plans for future development. In closing, he reviewed the life-work of the late Herman Frasch and proposed a silent toast to the memory of the Institute's most distinguished colleague and member. Prof. Withrow talked on the plans of the Committee on Education and the encouraging prospects of cooperation with the Carnegie Foundation for the Advancement of Teaching. Prof. Edmond O'Neill, of the University of California, spoke of the charms of his state and extended a most cordial invitation for the Institute to hold its convention there next year during the Panama-Pacific Exposition. After a speech by Prof. Olsen, on the work of the Institute, the banquet was voted the most successful ever held.

The most notable social feature of the meeting was the smoker, given at their home, by Professor and Mrs. Mason. The guests were received by Mrs. Mason, assisted by President Ricketts, Professor Green, Professor Mason and other members of the Polytechnic staff. Food and drink aplenty were provided and it is needless to say that this closing event of the Troy meeting was its crowning event.

## PAPERS

**Some Applications of Physical Chemistry to Industrial Processes.** By W. F. RITTMAN. The speaker developed the theoretical basis for a number of the well known processes, such as, contact sulfuric acid, air nitrates, Haber ammonia, producer gas and others, taking into consideration the equilibria, temperature and pressure factors involved. On the basis of the theoretical deductions, Mr. Rittman then calculated a number of the numerical factors and showed the striking agreement between them and the practical results already obtained. He briefly described and illustrated the application of this method

to investigations in new fields and referred to his recently published articles on Gas Reactions (see *THIS JOURNAL*, 6, 383 and 472).

**Studies on Filtration.** By J. W. BAIN and A. E. WIGLE. The authors presented the results of an extended investigation into the retention of moisture or solutions by various kinds, sizes and conditions of solids, in filtration. The results of this work will be of great direct benefit to engineers in estimation and plant design.

**Scrubber for Vacuum Apparatus for Laboratories.** By CHAS. BASKERVILLE. Professor Baskerville described and illustrated with blue-prints a complete installation of an apparatus for removing the corrosive gases, vapors, and moisture from gases in order to protect vacuum pumps.

**Some Professional Obligations.** By M. C. WHITAKER. Presidential Address, printed in full in this issue.

**Saratoga Septic Tanks.** By WM. P. MASON. Prof. Mason described the construction and operation of the Saratoga Sewage Disposal as a preliminary to a visit to the plant. He discussed the recent explosion of one of these large tanks and illustrated the results with lantern slides. He also reviewed the various theories offered to explain the explosion and advanced the new theory, which seemed to the members to be the most acceptable, that the disaster was due to an explosive mixture of septic gas or methane and air, known to exist in the tanks at times, ignited by a bubble of phosphine which has been noted in a number of places in decomposing sewage.

**Shoddy and Carbonized Waste.** By L. J. MATOS. The author discussed the commercial importance of wool recovery, outlined the methods generally used for removing vegetable fibers and suggested many new problems and fields yet open to investigation.

**Bleaching Cotton Fiber.** By J. C. HEBDEN. The speaker presented the results of extensive researches to determine the effect of the various steps in scouring and bleaching cotton fabric. He discussed in detail the difficult composition problems involved.

**Ozone in Ventilation.** By J. C. OLSEN and WM. H. ULRICH. Prof. Olsen reviewed previous contributions on this subject and presented the results of a most comprehensive quantitative study to determine both the oxidizing and deodorizing action of ozone; by his work, based upon such carefully planned and executed experiments, he has thrown much light upon the reasons which lie behind the mass of contradictory evidence recently published.

**The Present Patent Situation.** By MAXIMILIAN TOCH. Mr. Toch discussed the new rules for trial of patent suits and eloquently protested against the anomalous situation caused by the order to conduct the trial in open court before a judge when no provision has been made for additional judges to take this extra burden from an already heavily overworked bench. The speaker approved the new rules but lamented the shortsightedness and parsimonious attitude of our government which ignores the rights and interests of the owners of intellectual property.

**Patent Abuses.** By M. H. ITTNER. The speaker characterized patent pirates and patent sharks as parasites of industry. He illustrated this point by citing a case in which a field was "bottled up" as a result of the refusal of a larger industry to buy up a few patents. The paper was referred by vote of the convention to the Committee on Ethics of the Institute.

**A Combination Water Softener and Storage Tank.** By L. M. BOOTH. Mr. Booth described some large industrial and railroad installations recently made and illustrated with lan-

tern slides the details of construction and operation developed for these plants.

**Development of Rotary Furnaces.** By R. K. MEADE. This paper, which was illustrated by slides, discussed the historical development and uses of rotary furnaces and presented some interesting recent applications in various industries.

#### EXCURSIONS

The local committee had provided opportunities for a number of most interesting and instructive excursions. At the conclusion of lunch on Wednesday, the members inspected the buildings, grounds and laboratories of the Polytechnic Institute, after which they went to the Watervliet Arsenal, where they were met by Colonel Gibson and Major Brinker. By special arrangement, the visit was so timed that the members saw the shrinking on of the outer jacket of a 14-inch coast defense gun. Various other operations in the manufacture of heavy ordnance were observed and special demonstrations of recent models were provided by the officers in charge.

A special car was provided to take the visitors to Schenectady and from there to Saratoga and return to Troy.

**General Electric Company Works, Schenectady.** The members spent several hours in this plant under the guidance of men assigned by Dr. Whitney from the Research Laboratory staff. The new research laboratories proved to be the point of greatest interest, although the party visited all of the manufacturing departments. At the conclusion of the trip through the plant the members were entertained at luncheon by the General Electric Company.

**Saratoga Septic Tanks and Sewage Disposal.** The delegates went to Saratoga in their special car and were met there by Dr. Chas. Ferris, Medical Director of the New York State Reservation Commission, and a body of local physicians and taken in automobiles to inspect the sewage disposal plant. At the conclusion of this trip the entire party proceeded to visit the various springs and inspect the work of the Reservation Commission. The visitors were greatly impressed with the work accomplished and the plans now under way for the development of Saratoga as a resort.

**West Virginia Pulp and Paper Company Plant, Mechanicsville.** The visitors were here shown both sulfite and soda processes for making pulp, the making of paper, black ash recovery, etc. They were especially favored in seeing the large installation of Hargrave-Bird cells for carbonate and chlorine, the kilns for lime, the bleach plant and a most elaborate water-power equipment.

**The Geo. P. Ide Plants.** Two large shirt and collar factories of this company were visited. The officials showed every detail of their operations and the visitors found much of interest in the highly developed machinery and the laundering operations.

**Burden Iron Works.** The puddling process for the manufacture of wrought iron was demonstrated in this plant.

The Cohoes Filter Plant which uses mechanical filters, the Freihoffer Baking Company Plant, and the Albany Filtration Plant which has slow sand filter beds and mechanical scrubbing filters, were also open for inspection.

#### PRESIDENTIAL ADDRESS

##### SOME PROFESSIONAL OBLIGATIONS

By M. C. WHITAKER

Chemical Engineering as an organized profession is comparatively new, although many men have been engaged in this class of work since the beginning of large scale manufacture. Since the organization of this Institute, various definitions have been

given to outline the scope of our professional activities, many schemes have been suggested to improve the training of our apprentices, some advances have been made towards standardization in our engineering practice, a code defining the ethical standards of our profession has been formulated and adopted, and we have shown our aims, with some results, in constructive patent reform. Work of such a character is of the greatest importance, and is far in advance of that heretofore undertaken by any other organization in our field. It can never be regarded as completed, and the best thought and effort of well constituted committees will continue to be given to advancement along these lines, with great resultant benefit to the profession.

There comes a time, however, in the life history of every organization or enterprise, when the greatest advancement and improvement may be made by a process of introspection. It would seem to the speaker that chemical engineers might now, with great profit to themselves and benefit to the profession, submit to a process of self-analysis. Obviously it would be out of time and place to attempt now a profound or philosophical analysis of our internal personal relations and aims, but it is hoped that by reference to a few of the more fundamental points, we may thereby catalyze some productive reactions.

Chemical Engineering must, sooner or later, come to be recognized as the leader among the engineering professions. Its interests are larger and more varied, and its scope is greater and more intimately related to social and industrial progress, than that of any one or all of the other branches of applied science. Manufacturing output in the United States, which in money value is already almost equal to the largest single productive interest, will be dependent in some, if not in all, of its steps, upon the Chemical Engineer. The burden of the development of the industrial processes and the operation of the plants will fall upon him, and naturally the rewards of success and the odium of the failures will be his. The realization of the opportunities of such a profession, so full of brilliant promise and great possibilities, will depend in a large measure upon the breadth of view adopted in the acceptance of our responsibilities.

A voluble assertion of our importance will not give us the power to master our calling. Professional prestige, in the engineering field at least, is built upon achievement. Achievement worthy of the dignity of a profession cannot be built upon independent work, the spectacular results of a few individuals, or the hit-and-miss strokes of fortune. It must be based upon a consistent development of and by a body of able progressive men, and be based upon years of unselfish constructive coöperation, in which each member contributes his share, and in turn, draws freely from the common store.

The legal, the medical, and the clerical professions have devised for themselves some form of legal protection. The engineering professions, on the other hand, are subject to no form of external control, and may become self-developing or self-effacing according to the wisdom of the policies adopted in their direction and development, and the positiveness and value of their achievements. Merit, after all, is the only measure of success in engineering, and all failures, and even doubtful results, are promptly charged up against the profession.

The civil engineer may design and build a bridge. During construction, his work is open and in full view of the public and his colleagues. There is not a single feature of his purpose, his design, or his materials of construction which is not common knowledge to anyone who takes the trouble to look at his work, or read any of the numerous articles published during its progress. Even the lay public may be interested and pay their tribute to the man behind the work. The finished bridge stands in public as a monument to the power and ability of the builder and the profession he represents.

The mechanical engineer may design and build a wonderful machine. There is no secret about any of the features. His

colleagues, the public, or anyone may study and criticize his work, accept and profit by his suggestions, and ingenious features or may avoid his mistakes. The mechanical engineer has profited by the successes and failures of his predecessors in the art, and his successors, in their turn, will build better as a result of his work.

So it is with the mining and the electrical engineer. Each works with a full knowledge of what has gone before; each contributes his share to the advancement of his art, and the standing of the professions is enhanced because of his contributions.

The chemical engineer, on the other hand, works in unappreciated silence behind factory walls. He is not building a monument which invites public approval, though he may be making a product of equal value and more wonderful if it were understood. The details of his work are carefully guarded, and he is even denied the stimulus of public interest in his achievements. His designs, materials and methods often lack the helpful suggestions of his fellow engineers. He may repeat at great expense the mistakes previously made by his neighbor, or may fail to avail himself of well worked out methods which are unknown to him on account of lack of proper exchange of professional knowledge. If he is secretive, it comes as a result of environment and conditions. This secretiveness often becomes a habit, and is assumed to be a necessity. At times this habit is extended either unconsciously or accidentally to ludicrous limits. For example, note how difficult it is to find the professional or business connections of a chemist or chemical engineer. Surely there is nothing about this which should be concealed. On the contrary, good would result both to him and his employer, by having his connections and field of activity well known. The directories of all other engineering societies contain valuable information about the professional activities of their membership, while our directories in many cases carefully disguise even the business addresses of our members.

The Chemical Engineer's efficiency in the production of successful results is reduced to a minimum, because of a lack of liberal professional coöperation, while civil, mechanical, electrical, and other engineers are steadily improving their professional efficiency by a systematic exchange of principles and practices, and a selective action to carry forward the good methods and reject the bad ones. We, of the Chemical Engineering profession, are harboring conditions which retard or frequently even prevent professional progress.

When the work of the Chemical Engineer is not open to public view, his productive efforts are not understood, and, therefore, not appreciated, his achievements cautiously guarded, his business connections withheld from the directories of his societies, and absolutely no record of his professional activities is made available, is it any wonder the lay public usually think of him as a druggist?

If one traces the life history of the development of the Chemical Engineer, it will be found that we have some bad traditions to overcome. Our alchemist forefathers cultivated secretiveness, mystery and even deception. These dark art traditions are openly professed today in some of our factories, while in others they remain in latent evidence.

With these adverse conditions and traditions in existence, it would seem that the Chemical Engineers are confronted with an important problem which intimately concerns the progress and development of the profession. Inefficiency and loss of prestige are bound to result from unsupported individual effort. Coöperation is essential to substantial engineering development. This coöperation comes about naturally in other engineering professions, and it will have to come, if not naturally, then by force of necessity, in ours.

Every failure in design, every fatal accident, every industrial disease, every fire or explosion in a chemical works, every com-

mmercial insuccess is an indictment against the chemical engineering profession. Cause and effect in bridge failures, dam failures, boiler explosions, railroad and steamship wrecks, are freely discussed in conventions and journals, for the benefit of the interested profession. These open and frank discussions disarm public criticism on the one hand, and on the other, place before all members of the profession most impressive and profitable lessons in what not to do.

The Chemical Engineer in such cases, apparently guided by his ancient traditions, or his environment controlled habits, as no other motive seems discernible, often secretes the facts not only from the public, but also from his professional associates. Such secretiveness always arouses public suspicion. The interests of humanity may be sacrificed, and the profession, without the knowledge of what has happened, may go blundering into the same disaster again and again. These costly disasters are not even recorded as experience outside of the factory walls in which they occur.

Have the Chemical Engineers discussed or even heard of the causes leading to the failure of the coke plant at Bethlehem; the cause and effect of the explosion in the artificial leather factory at Detroit; the lessons to be drawn from the recent fire in the Mallinckrodt works in St. Louis; the cause and effect of the failure of a large gas holder at Philadelphia; the cause or remedy of the large number of industrial diseases in some of our plants; the complete failure of this or that piece of equipment or method of installation?

Do the affected or afflicted Chemical Engineers seek the assistance of their associates and professional colleagues in determining the cause, and suggesting the remedy for such disasters?

If the cause and the remedy are determined, are the facts made public?

Think of the benefit which would come to our profession and to humanity and industry in general, from frank authoritative discussion of these and many other problems which come within the experience of every Chemical Engineer. The discussion of the defective design, or material, or installation of chemical engineering appliances is a thing which would be of inestimable benefit, not only to other engineers, but also ultimately to the producers of the appliances. Negative results can be of no possible value to those industries which have developed them, but if they were published or discussed, they would become of the greatest importance to future engineering progress. Why should they be jealously guarded and secreted and the progress of this profession thereby blocked?

The question as to what knowledge the manufacturer should disclose for public use, and what should be kept within the factory walls is one which may be settled by the rule of reason, but never settled by yielding to the inclinations of our natural environment and our ancestral traditions. When it becomes clear that these conditions are blockading engineering progress and our own professional development, it will not be simply a duty, but an obligation, for every Chemical Engineer to apply this rule of reason.

Property value might safely be accepted as the basis for determining what should, and what should not be disclosed. Manufacturers and Chemical Engineers would not be expected to give out unprotected information of direct property value, any more than civil engineers would be expected to publish their working drawings before the contracts were awarded, or the mechanical engineer be expected to give away the appliances in which he had invested his time and his money. Such a policy would result in commercial anarchy, and tend to destroy industrial stability, and with it the dependent professions.

Fortunately it is very often the knowledge having the least property value which, when collected and classified, possesses the greatest professional value. Negative results can usually be disclosed without loss, and they form the most substantial basis for engineering development.



On the other hand, the publication of the failure of a design, a material, or a process, would invite constructive thought from others, which might turn a failure into a success, or suggest to our young investigators researches which would definitely establish or disprove the scientific validity of the principles involved.

The interests of humanity demand that industrial diseases, industrial accidents, and improvements in working conditions be openly and frankly discussed, in order that the combined effort of all minds be brought to bear on the needed solutions. Proper publicity in all bad or doubtful cases, would do much to soften the hearts of the financial control, and at the same time independently enlist the services of the physiological chemists, the medical researchers, the mill designers, and many minds in our own profession, which is most seriously indented.

We have all heard the statement, by members of this profession, that there are no adequate textbooks, or handbooks in Chemical Engineering, of the same standard of excellence as those existing in mechanical engineering, for example. Such books, in any engineering field, are the results of compilations and classifications of approved matter from current technical journals, and Society proceedings, and it is inevitable that they will be large or small, dense or rare, profound or superficial, in direct proportion to the current available material.

If we secrete our information, or fail to publish our researches, hoard our knowledge and avoid the full and frank discussion of our industrial problems, we are bound to reap the negative rewards. Our books will not represent the sum of a profession's knowledge, but instead, the comparatively small, laboriously attained work of one or a very few individuals.

This Institute, representing as it does the leading organization devoted exclusively to developing the technical interests of the Chemical Engineers, and enhancing the prestige and value of that profession, should be the first to consider all obstacles to

the accomplishment of its purpose. Our profession is built upon the applications of a science of the most infinite and varied detail. The mastery of modern chemistry requires a highly developed mind, and one which should be fully qualified to attack and solve with ease the general problems of policy in the development of the profession. Our organization is new, and the problems are large and numerous. Most careful consideration must be given to the direction of our energies into those channels in which we shall find the most productive returns. We have no time to waste on philosophical quibbling or fussy arguments. If self-analysis shows that the indictment of narrowness is valid, and that the best interests of our profession will be served, as I think they will, by a more active interest in public questions, such as the so-called conservation movement, public service control, corporate regulation, financing of industrial enterprises, etc., then we should study and discuss these problems in our meetings and proceedings.

If Chemical Engineering education is twenty or thirty years behind the methods and efficiency of mechanical and electrical engineering training, as I think it is, and its improvement is being blocked by the dogmatic teaching that chemical manufacture is nothing more than enlarged laboratory practice, it then becomes evident that even more strenuous efforts will be required, from this Institute and its hard-working committees, to produce the desired results.

If, as I firmly believe, our professional progress is being seriously blocked by an unjustified and unjustifiable veil of secrecy or mystery drawn around our experiences, our needs, our achievements, and our professional activities, the removal of this obstacle to our advancement becomes an obligation upon each constituent member of the Chemical Engineering profession, and particularly upon the Institute of Chemical Engineers.

CHEMICAL ENGINEERING LABORATORIES  
COLUMBIA UNIVERSITY, NEW YORK

## NOTES AND CORRESPONDENCE

### THE INVENTION OF CELLULOID<sup>1</sup>

I discussed quite fully the question of priority of invention of celluloid, when, as your representative, I handed to Mr. John Wesley Hyatt, the Perkin Gold Medal, on the evening of January 23rd last, and as my remarks were printed in full in *THIS JOURNAL*, 5, 156, I do not think it necessary at this time to go over the ground again. There are, however, a few points to which it seems proper to refer. My friend, Dr. Schüpphaus, lays considerable stress on the fact that he has had thirty years' experience in the celluloid industry; this is, indeed, a long period.

My familiarity with pyroxylin began about 1851, when I was a boy fourteen years of age. As a pupil in the New Bedford High School, just beginning to study chemistry, I began to make chemical experiments in my workshop. My sportsman uncle, who had been experimenting with guncotton of his own make in his rifle, turned over to me a large green bottle of strong nitric acid and another of fuming sulfuric acid. I quickly learned to make explosive guncotton, and did things with it I should hardly have the nerve to do now. For example, I would place a tuft of guncotton in the palm of my hand, cover it with gunpowder, leaving a few of its fibers protruding, and then light it with the red hot end of a match. The cotton would explode leaving the unburned gunpowder in my hand. My sister happens to be present here tonight, and she remembers well how I used to startle her and my younger brother, and dear old grandmother, by flashing trains of guncotton on the parlor table.

In 1857, I took up amateur photography and made my own

soluble pyroxylin and collodion. Since that time I have acted as expert in several investigations involving pyroxylin, explosives, varnishes, etc., and in June, 1881, testified in the suit of Daniel Spill against the Celluloid Manufacturing Company. During recent years, I have had occasion to look up the history of pyroxylin plastics as expert in the Kodak film case which was recently decided. But in forming an opinion on the subject under discussion, I do not rely on my own experience. The issue is a matter which must be settled by facts. Dr. Schüpphaus began his address by saying that he wrote the article on Celluloid in Thorpe's "Dictionary of Applied Chemistry," "from which Prof. Chandler submits a mangled quotation with his emphatic disapproval."

Of course, I pardon my friend's use of the word "mangled;" his imperfect knowledge of the English language has led him to use a word which generally means cut or lacerated, as the "mangled remains" of a person who has been run over by a railway train. In German the word implies deficiency, and the doctor evidently uses it with that significance. My quotation was verbatim as follows: "The substance was first produced by Daniel Spill, of Hackney, England, and came into commerce under the name xylonite." "Spill's method of converting the nitrocellulose has been followed for more than forty years." A verbatim quotation of two entire sentences can hardly be said in English to be "mangled." In the first edition of Thorpe's Dictionary, the credit of first making celluloid is given to Hyatt.

Further, my friend Schüpphaus seems to err in the use of the word celluloid, by making it include plastics containing not only pyroxylin and camphor but a variety of other substances such as animal and vegetable oils, gums, resins, etc., such as were

<sup>1</sup> Remarks of C. F. Chandler at meeting of the New York Section of the Society of Chemical Industry, The Chemists' Club, April 24, 1914, in reply to Dr. Robert C. Schüpphaus, (see *THIS JOURNAL*, 6, 440).

made by Parkes prior to 1855 and later by his pupil, Spill, who became associated with Parkes in 1864 in the Parkesene Co. They did not call their product "celluloid," and I have seen no evidence that leads me to think that they ever made celluloid, till after Hyatt made it, and a man who learned the process from Hyatt, later entered the service of Spill.

There is another thing which perhaps Dr. Schüpphaus does not understand—the American conditions on which patents are granted. They are quite different from those that prevail in England. In the United States, the original inventor is alone entitled to a patent and if a man who is not the original inventor secures a patent, it becomes null and void when it is shown that he was not the inventor. In England it is quite different. On March 23, 1876, Daniel Spill's Bill of Complaint against the Celluloid Manufacturing Co. was sworn to, and promptly filed in the Circuit Court of the United States. Spill came over himself, employed the best patent lawyers, testified himself, produced many other witnesses, took testimony in London by Commission, and spent eight and a half years in vain trying to prove that the Celluloid Co. infringed his patents. The weakness of his case is shown at the outset. With all his patents and those of Parkes, he was only able to charge two infringements: (1) The use of camphor and alcohol solvent under Patent 97,454 of 1869; (2) the bleaching of pyroxylin under Patent 101,175 of 1870. The case was argued before Judge Blatchford, one of the most eminent United States judges, especially experienced in patent litigation. In his opinion given May 25, 1880, he decided that the defendant, the Celluloid Co. had failed to prove that Spill was not the first person to use camphor and alcohol to dissolve pyroxylin, or that he was not the first person to bleach pyroxylin. He declared both patents valid, and awarded to Spill recovery of profits and damages, to be ascertained by reference to a master, and a perpetual injunction. The injunction, however, proved inoperative, for when the Celluloid Co. continued to manufacture and Spill's counsel made a motion to punish the company for contempt, the company showed that it had given up bleaching pyroxylin, and had substituted methyl alcohol for ethyl alcohol. The court ruled that this was a valid defense and that the company was not in contempt—so they continued to manufacture. In the meantime, the plaintiffs proceeded to prove damages and profits and the defendant company put in further evidence in defense. On February 25, 1884, the master filed his report, stating that Spill's lawyers had failed to furnish the necessary data to enable him to report any profits, or to fix any damages. Spill's lawyers claimed \$276,667.66 on account of the alcohol camphor patent; \$504,306.25 on the pyroxylin bleaching patent. The litigation was continued, more testimony was taken by both sides, and on August 21, 1884, Judge Blatchford did what required great moral courage. He reversed his original decision against the Celluloid Co. He decided on the testimony and documents presented that Spill's patent 97,454 was invalid as far as it claimed the use of camphor and alcohol as a solvent for pyroxylin, for the reason that this invention was made by Parkes. Further, he decided that Spill's Patent 101,175 was invalid as far as it claimed bleaching pyroxylin, as that is not a patentable invention.

Now I do not think that either Dr. Schüpphaus or myself competent to reverse the final decision of Judge Blatchford, reached after eight and one-half years of litigation in which Spill had every opportunity to prove his case. He certainly failed to prove that he invented celluloid, or, that Hyatt's company had appropriated anything that he had invented.

C. F. CHANDLER

51 EAST 54TH STREET  
NEW YORK

#### SYMPOSIUM ON THE RECOVERY OF WOOL GREASE

*Editor of the Journal of Industrial and Engineering Chemistry:*

As a casual guest of the New England Section of the Society of Chemical Industry, I was much interested in the program of

the recent meeting held in Boston, at the Engineers' Club, on May 15, 1914.

Mr. H. W. Clark, Chief chemist of the Mass. State Board of Health, read a short paper on the "Prevention of Stream Pollution," giving in clear and condensed form the substance of the history of the legislation and work of the State in the correction of stream pollution in general, and of that caused by wool grease in particular.

This was followed by a crisp, concise statement from the practical side, by Mr. Joseph Edmondson, of the Barre Wool Combing Company, on the "Operation of Wool Grease Recovery Plants in England," and fortified by a description of the same as used at the Barre mills. The speaker contrasted the low wages of England with the higher and almost prohibitive wages of America; and emphasized the difficulty of meeting expenses on this basis. The recovery of wool grease in England seems to have been developed, not as a profitable matter in any case, when considering the original taking out of the grease, but solely as a necessary requirement of the laws against public nuisance.

Prof. R. S. Weston, consulting sanitary engineer, and teacher of sanitary engineering in the Massachusetts Institute of Technology, presented an admirable paper on the "Engineering of Wool Grease Recovery Plants," showing the figures for the actual operation of a plant of his designing at the works of the Hudson Worsted Company; this was illustrated by lantern slides. Mr. Weston also emphasized the financial perplexities of the problems, as it appears that the returns can meet only the charges for acid and labor, with no chance to make good on the equipment. The Hudson plant uses what is essentially the English method of acid-cracking, and pressing. In his later remarks, Mr. Weston briefly discussed several other processes such as the Smith-Leach, the Battage, etc., and cautioned against accepting all of these foreign recommendations without careful testing, as they do not always seem to give satisfactory results in America.

Mr. C. E. Swett, of A. D. Little, Inc., of Boston, gave a good history of some of the more important attempts to recover wool grease in America. Mr. Swett regarded the whole wool grease extraction question as one not of financial promise, but entirely necessary for the meeting of the removal of public nuisance. He noted some details of the Yorkshire method, and called attention to the "colloids" which in some cases resist the clean and easy clarification of the liquors. He also noted, but without detail, the "naphtha" process, as practiced by the Arlington Mills, of Lawrence, commenting on the good quality of the tops and the grease.

Mr. H. Gardner McKerrow, of the Textile Importing Co., of Boston, then discussed "The Market for, and Marketing of, Recovered Grease," in an eminently interesting and instructive manner. Mr. McKerrow gave much valuable information on the variety and price of the grease products, and also explained the almost successful working of the Smith-Leach process in England; it appears that a firm which exploited this process, was compelled, by business conditions, to change from high-grade Australian wool to other lower grades, which are not so well adapted to yielding good results with this process; so that we are not to argue against the process necessarily from that trial. Mr. McKerrow incidentally called attention to the possible use of a very dilute emulsion of wool grease with soap and cheap molasses, for a satisfactory road dressing.

In leading the discussion, Prof. W. H. Walker, of the Massachusetts Institute of Technology, discussed some of the aspects of the distillation of wool grease; and while frankly acknowledging the difficulties, still believed that it is quite feasible to meet and overcome all the incidental obstacles in this line.

Mr. W. H. Butler, of the W. H. H. Slack Co., of Springfield, Vt. (shoddy), gave some interesting remarks from one who, evidently, has seen personally much of the practical and business side of textile work; and incidentally defended the use of mineral oils with wool, on which point he met some support and much



criticism from other speakers. He also approved the use of wool grease products for oiling wool, as it seemed to him to be the "natural" and suitable product for wool. Mr. Butler did not think that the naphtha process was good for wool, as it leaves it somewhat wiry and stiff from excessive degreasing.

There were other speakers; but the general tone of the meeting, in spite of the excellent character and brevity of the papers, was that the recovery of wool grease is not one of profit, but a sanitary necessity. This is probably true, as far as actual history to the present is concerned; but there were some present who think that the subject was not fully developed as it should have been, and as it needs to be shown, and especially in view of the urgent need of more modern methods to meet urgent conditions. Thus, it is quite surprising that no concise statement was given by any one as to the actual chemical composition and ingredients of commercial dégras, wool grease, etc. Indeed, the only speaker who touched on the commercial ingredients of wool grease, was not a professional chemist, but the practical and able man of business, Mr. McKerrow. Moreover, there was no detailed reference to the solvent processes and their great possibilities. The Arlington process was mentioned, but there was no reference to the well-known Tacony process, of the Erben-Harding Co., of Philadelphia, with their also well-known high quality of tops.

In a word, it is the conviction of the writer that the future line of progress is clearly pointed out in the improvement of the Arlington and Tacony processes, so that they shall give a flexible process, capable of degreasing the wool to any desired degree. Further, till this is done, there is certain to be much opposition from the practical mill men who see, in the naphtha process tops, wool which has been rendered too wiry and "staring." Moreover, there is every probability that this same despised two-cent wool grease will prove one of the big bonanzas of trades wastes. We hear much of the brilliant invention and thrift of this age; but it is probable that the coming generations will refer to this as an age of waste and stupidity. Perhaps there is no fairly abundant waste "grease" product which is so full and rich in the as yet undeveloped variety and desirability of its possible extractives as wool grease. It is not to the credit of the industrial chemical engineer if he shrinks from this difficult but promising task of converting trouble to profit.

The meeting was a good one; and in spite of the generally depressing tone of the actual financial loss in recovering wool grease, much will come from focussing the attention of determined workers on this unique field of trade waste.

NEWTONVILLE, MASS.  
May 18, 1914

CHARLES S. PALMER

### GUARANTEED CHEMICALS

*Editor of the Journal of Industrial and Engineering Chemistry:*

During the past fifteen years an attempt has been made to place in the hands of the chemists reagents with an advertised purity. The following is a typical example of some of the statements: "The term 'C. P.' by itself is almost meaningless, but when accompanied by our ACCURATE analysis it becomes a guarantee of purity."

Advertisements of this character are likely to lead the chemist into many pitfalls, the implication being almost, if not quite, a guarantee of purity. The chemist who is reasonably conscientious will always ensure for himself that his standard conforms to the purity he desires by making with his own hands the tests that should be applied. But unfortunately many chemists choose the easier course of accepting the published "guarantee" or "analysis."

Those who have had the opportunity of looking into some of these presumably high-quality reagents, find C. P. sodium hydroxide, stated to contain a trace of carbon dioxide, to contain as high as 10.31 per cent CO<sub>2</sub>.

Petroleum ether, stated to boil at 40°, actually boiled between 40° and 80°, and contained a large amount of insoluble and a still larger amount of non-volatile matter.

Ether labeled "Absolute Ether" contained both water and alcohol, and washed ether contained alcohol.

A lot of sodium bromate labeled "Bromide . . . . None" in various samples contained 42.9 to 54.2 per cent sodium bromide.

A lot of bromine was marked "C. P., Cl 0.11%–0.46%." When the distributor was asked by what method the chlorine content was determined, he wrote: "In reference to the method of testing chlorine in bromine, the analysis which we gave was furnished us by the manufacturers. We never made an analysis of it ourselves which is very difficult, and we are, therefore, unable to give you any more definite information."

The following label is interesting:

COPPER METAL, SHEET			
Analysis			
Per cent			
Fe . . . . .	0.001	Sb . . . . .	None
Sn . . . . .	None	Cu . . . . .	None

The above errors in labeling reagents certainly are not a justification for the advertisement "The ACCURATE analysis shown on the label of every bottle of our chemicals is an absolute guarantee of their quality."

On taking up the general question of Analyzed Chemicals with the Bureau of Standards, the following was received under date of March 31, 1914: "You are not alone in your troubles with analyzed chemicals. We never take at their face value the statements on the labels, and often find them absolutely false. Others have had the same experience. This holds for reagents of foreign as well as domestic make."

Secretary of Commerce Redfield writes me under date of May 18, 1914: "The Bureau of Standards and other laboratories, governmental as well as unofficial, are convinced of the desirability of some action which shall ameliorate existing conditions with regard to reagents, but their efforts in this direction should be reinforced by the testimony and support of all who have cause for complaint."

This whole subject of the labeling of pure chemicals is obviously a very important one, particularly so in such legal work as is constantly being done under The Pure Food and Drugs Act and under the various States Pure Food Laws. The most important testimony given under these acts is unquestionably the analysis of the chemist, and if he does not ascertain for himself the quality of the standardizing materials and reagents, grave errors may be committed.

It would be most unreasonable for the chemist to expect a guaranteed chemical to have so high a degree of purity that it could be used in atomic weight determinations, but the chemical world is certainly justified in asking for a purity within at least a few per cent.

UNIVERSITY OF WISCONSIN, MADISON  
May 27, 1914

VICTOR LENHER

### TOXICITY OF VARIOUS WOOD PRESERVATIVES—A NOTE

*Editor of the Journal of Industrial and Engineering Chemistry:*

In THIS JOURNAL, 6, 128, appeared a paper by C. J. Humphrey and Ruth M. Fleming under the above title which I believe is likely to be rather misleading even though the writers appear to be anxious to prevent any misconception that may arise from their results in so far as they state that "the toxicity of a given substance is not necessarily an ultimate criterion of its service value." But the mere fact that they have published their results indicates that they attach considerable value to them, and since furthermore they say that the toxicity "when correlated with other suitable properties, such as cost, ease of injection, etc. . . . . assumes high importance in influencing our judgment as to what may normally be expected from the substance,"



it is plain that they consider this toxicity test as made by them to be of value in judging a wood preservative. Careful study of the method employed in this toxicity test and of the results obtained has led me to the conclusion that the method employed is misleading and the conclusions reached not acceptable. My reasons are the following:

The results of this test would indicate that carbolic acid is the most valuable component of creosote oil for wood-preserving purposes and that the high boiling fractions are the least valuable. In this respect these tests flatly contradict the results of years of experience and of careful investigation which have proven almost beyond a doubt that the highest boiling fractions of coal tar are the most valuable components of creosote for wood preservation, and that the low boiling fractions, particularly the carbolic acid and naphthalene, are of relatively little value because they do remain in the wood but a comparatively short time—they volatilize. The same conclusion which this toxicity test leads to was reached years ago by the early advocates of creosote oil for wood preservation who were led to this conclusion by their general knowledge of the toxicity of carbolic acid and naphthalene. Hence, for years, creosote specifications called for large quantities of carbolic acid and naphthalene and they neglected or almost rejected the high boiling oils. The error involved in these specifications was discovered only through long years of trial and observation—nothing but a great mass of facts to the contrary convinced wood preservers of the error of specifying definite amounts of carbolic acid and of naphthalene. The reappearance of this former error in this new garb should not be permitted.

The authors appear to be desirous of avoiding this old disproven conclusion since they say that the toxicity test "is not necessarily an ultimate criterion, but when correlated with other suitable properties such as . . . permanence . . . it assumes high importance." But it appears to me that they should have safeguarded this point by proper experimentation. Thus by making the toxicity test also on samples which have been previously subjected to a "permanence" test (*e. g.*, an evaporation test) they would have correlated the toxicity and the permanence test in the most desirable manner. Had the authors done this, the above conclusion which contradicts the world's experience would probably not have been reached.

The results presented in the publication do not appear to harmonize among themselves even. Thus fuel oil is reported as having a toxicity such that a concentration of 6 per cent is required to kill *Fomes annosus*, while the same sort of an oil with an addition of a little of a copper salt (probably copper oleate, which if it has any effect should increase rather than decrease the toxicity) requires a concentration of 35 per cent to kill the same fungi. Again, the fraction which was obtained by distillation from a certain coal tar oil between 275° and 315°C., required a concentration of 33 per cent to kill the fungi used, while the three carbolineums mentioned (which are practically nothing but the same high boiling fractions of certain coal tars) appear so much more toxic that a concentration of only one-half per cent of one of these carbolineums was sufficient to kill the fungi and none of the carbolineums required more than 5 per cent. Although a difference in the toxicity of corresponding fractions from different coal tars probably exists, yet it would be surprising that the authors should have chosen a coal tar oil so greatly different from the great mass of the best coal tar oils as these results indicate; and if they have chosen so greatly different a coal tar oil, then they are scarcely justified in making the general conclusion which they have made from this special sample: "This indicates the advantage from a toxicity standpoint, of removing at least a part of the heavier tar oils" (from creosotes). Assuming what is more likely to be true—namely, that the creosote oil used in their experiment was a fair representative of oil of average quality, then it appears that the re-

sults obtained with the 275–315° fraction and the results obtained with the three carbolineums are too far apart to be correct.

The discrepancies just pointed out are probably due to the fact that the emulsions of these oils are not true solutions but colloidal solutions. It is tacitly assumed in the publication under consideration that the oils emulsified by means of gum arabic form true solutions and that hence their activities are proportional to their concentrations. This is a vital mistake. The activity of a substance in a colloidal solution or mixture is not only less than it would be in true solution, but it varies greatly with the state of aggregation that any particular substance assumes in this sort of mixture. Even the activities of emulsions of such closely related substances as high and low boiling tar oils are probably not proportional to their activities under other conditions because the states of aggregation in colloidal solutions vary particularly with the surface tensions and viscosities of the components, and different tar oils vary greatly in these respects. If the states of aggregation are different—that is, if in one case the oil particles are relatively larger or smaller than in another case, then the ratio of distribution between the oil phase and the water phase in one case is different from that of the other, and hence the activities or effects of the oil in these emulsions is not a measure of their effect under other conditions. This I believe is the cause of the discrepancies pointed out above, and it appears to me that in any case it casts serious doubts upon the validity of the results obtained with this method.

UNIVERSITY OF TEXAS, AUSTIN  
April 23, 1914

E. P. SCHOCH

#### NOTE ON MEANING OF "IMPURITIES" AND HOW THEY SHOULD BE DETERMINED IN GREASE, TALLOW, ETC.

*Editor of the Journal of Industrial and Engineering Chemistry:*

The writer proposed, at the New Haven meeting of the American Chemical Society, some five or six years ago, that the Committee on Fats take up this question and try to work out and get adopted, some standard meaning and method for the determination of this much misunderstood term in fat analysis. So far as I know, nothing has ever come of this suggestion, and there is nothing that is causing so much dispute between merchants and chemists and among the chemists themselves, who have to deal with this subject, as this point.

The term should properly mean, "anything in the fat (outside of water and unsaponifiable which are both taken care of) that does not saponify and make soap" (of course, omitting the glycerine). The general understanding is that "impurities" shall be determined by getting the "insoluble in cold gasoline." This is all right when metallic soaps are not present, but when they are, the "insoluble in cold gasoline" may mean anything. In the first place, if 10 per cent lime soap is present, and there is frequently this much in bone or glue greases, if we actually get the insoluble in cold gasoline, it would take some two days' work and use about a gallon of gasoline, that is, if the grease were dissolved in cold gasoline, filtered through balanced papers (folded double) and then washed on the paper till free from grease. If the nearest approximation of the actual amount is desired, this is the most accurate way, but this is only an approximation as it is impossible to get at some of the grease occluded in the lime soap, and also some of the lime soap is dissolved in the gasoline. Another method used by some chemists is to dissolve the grease in hot gasoline and let stand a couple of hours on the assumption that all the lime soap will precipitate. It is then filtered, put in the bath to dry, rewashed three or more times, drying between each washing and finally called complete. This method is absolutely inaccurate, because in the first place the lime soap will not all precipitate after having been dissolved in

hot gasoline and secondly because each time the insoluble is dried in the bath, the lime soap melts and is then more or less soluble to the subsequent washings, so that a grease testing 10 per cent by the first long drawn-out method will give about 2 per cent by this other method, or if continued long enough will give practically no insoluble.

Some two or three years ago the writer received from A. Norman Tate & Co., of Liverpool, their method, which is to dissolve in hot gasoline and wash, leaving behind only the actual dirt; an ash determination is then made and the dirt and ash called the "impurities." In the writer's opinion, this is the only logical method as it includes everything not available for soap-making, for the fatty acids combined as lime soap are available and hence should never be considered as impurity. If the client wants the lime soap included, it can be determined by calculation from the amount of lime present.

One reason, aside from its undoubted superiority, for using the method just mentioned, is that Tate's tests are official (practically) in all foreign countries, and all export grease is likely to come under his test. With our chemists using all kinds of methods, endless differences and disputes are always arising that are very bad for the profession as it is impossible to get the average grease broker to listen to any discussion of differences in methods.

76½ PINE STREET, NEW YORK  
April 5, 1914

A. G. STILLWELL

## TEST OF GILA RIVER NATURAL ALUMINUM SULFATE IN WATER PURIFICATION

The writer, in investigating the aluminum sulfate deposits of New Mexico, particularly that on the Gila River, in Grant Co., was impressed with the possible utility of this natural product as a coagulant in water purification and filtration. The assays and analyses seemed to assure the potential value of this product and it remained for a thorough practical test to be made under the exact conditions and requirements governing the use of the manufactured aluminum sulfate or similar coagulants, as used at the various water purification plants throughout the country.

The soluble sulfates of aluminum are found in the Gila River deposits in two forms, namely, alunogen, or hydrated aluminum sulfate with the theoretical composition:  $Al_2O_3$ , 15.3 per cent;  $SO_3$ , 30.0 per cent;  $H_2O$ , 48.7 per cent; and halotrichite, or sulfate of aluminum and iron with the chemical composition:  $FeO$ , 7.8 per cent;  $Al_2O_3$ , 11.0 per cent;  $SO_3$ , 34.5 per cent;  $H_2O$ , 46.7 per cent.

These tests were carried out under the personal supervision of Dr. Chas. P. Hoover, chemist in charge of the Columbus Water Purification Works, Columbus, Ohio, with the assistance of Russel D. Scott, Elmer J. Nealon and Walter L. Melick. The specifications for aluminum sulfate, as used by this plant, are as follows:

"The material shall be that known as basic sulfate of alumina containing no free acid. It shall be crushed into small lumps, ranging in size from  $\frac{1}{2}$  to  $2\frac{1}{2}$  inches and shall be free from chips and other foreign matter. It shall contain not less than 17 per cent available water-soluble alum ( $Al_2O_3$ ) and of this alumina content there shall be at least 3 per cent of its weight in excess of the amount theoretically required to combine with sulfuric acid present. The material shall contain not more than 0.5 per cent of matter insoluble in cold distilled water."

The halotrichite analyzed by Dr. Hoover was as follows:

$Fe_2O_3$ .....	4.14	Insoluble in water.....	0.48
$Al_2O_3$ .....	15.66	Loss on ignition.....	80.32
$SO_3$ .....	36.36	Basicity—plus.....	..
$H_2O$ .....	43.96		

Dr. Hoover concludes his report with: "I was not aware that a natural deposit of such magnitude and purity existed and these tests are very interesting to me as it is a first-class alum for water purification purposes. It contains no free acid and is very high in aluminum sulfate. This naturally would be worth, to us at

Columbus, \$17.00 per ton. We have also tried this material out on some of our samples of turbid river water and find that it coagulates well, and that for each grain of the material added per gallon of water, the alkalinity is reduced 7.5 parts per million. This is just about what is expected of a first-class filter alum. The Columbus plant is using about 1000 tons per year." The alunogen gives the same general results.

The samples were received at the laboratory, Dec. 18, 1913 and were the ordinary run of material, no selection having been made. Report was rendered Feb. 4, 1914.

The thanks of the writer are due the above-mentioned gentlemen for their generous cooperation and assistance.

5927 WALTON AVE., PHILADELPHIA  
May 11, 1914

D. M. GROSH

## THE EFFECTS OF THE ENSILAGE PROCESS ON THE SOLUBILITY AND METABOLISM OF FLOATS

*Editor of the Journal of Industrial and Engineering Chemistry:*

We note, with interest, the article by C. A. Mooers in the June number of THIS JOURNAL on "The Effect of Ensilage Fermentation and Animal Digestion on the Solubility of Phosphoric Acid in Phosphate Rock," in which he considers a previous article by the writer and C. M. Fritz on this same matter.

In order to correct an impression given by Professor Mooers's article we would state that our especial interest in the subject was as applying to animal feeding, that our one conclusion had reference to the bearing of our results on animal feeding, and that in our second paragraph we stated specifically: "We do not mean to suggest, however, that all of the floats which one might desire to add to the soil could, in this way, be passed through the silo and the animal."

Professor Mooers states that we "did not furnish the composition of the phosphate rock." He, therefore, assumes a phosphorus content for the floats which we used. To facilitate such a computation as Professor Mooers has made we submitted data on the floats, as follows: total phosphorus, water-soluble phosphorus and phosphorus soluble in 0.2 per cent HCl. These figures Professor Mooers seems not to have noticed.

Professor Mooers' results in the feeding of the phosphated silage to cows are of interest, and we accept without question his finding that a cow can not be expected to eat a pound of phosphate rock with the silage from each 50 pounds of green corn.

We do not follow Professor Mooers, however, in his conclusion that in the process of animal digestion there was reversion of the  $P_2O_5$  made soluble by the ensilage process. This conclusion is said to be based on "samples" of dung from each animal, and the assumption "that all of the phosphoric acid was voided in the dung." It also seems to involve the assumption that the phosphoric acid of the food passed through the animal without loss of phosphorus by absorption from the alimentary tract, and without gain of phosphorus to the contents of the alimentary tract in metabolic products, in fact that the normal physiological activity of the cow was suspended during this fertility investigation. It is also assumed that the rations involved in the comparison differed only in regard to the presence of rock phosphate, but the data submitted show marked differences in the proportionate amounts of the other components. And further, since the total amounts of phosphorus in the intake and in the outgo were in no way compared, it is impossible to say what the cows did with the phosphorus rendered soluble by the ensilage process. That this was readily absorbable stands without question; indeed a considerable proportion of the raw rock phosphate would be dissolved and rendered assimilable.

Is it not more likely that the cows absorbed and assimilated the soluble phosphate than that it "reverted?"

DEPARTMENT OF NUTRITION  
OHIO AGRICULTURAL EXPERIMENT STATION  
WOOSTER, June 17, 1914

E. B. FORBES

## MINE INSPECTORS INSTITUTE OF THE U. S.

## 7th ANNUAL MEETING—PITTSBURGH, JUNE 9-12

The 7th annual meeting of the Mine Inspectors Institute of the United States was held in Pittsburgh, Pa., June 9th to 12th. In his annual address, President Roderick referred to the last meeting in Birmingham, Ala., and the means and methods of preventing mine accidents were discussed by the hundred officials in attendance.

R. H. Beddow told of the disaster in a mine at Dawson, N. M., on October 22, 1913, in which 261 men were killed. He attributed the accident to the firing of a careless shot at a daylight hour when all the men were in the mines, in direct violation of the law. Papers of interest were presented by John Dunlop on "Booster Fans," and by J. P. Moore on "First Aid to the Injured."

On June 11th the members of the Institute witnessed an experimental explosion at the Bureau of Mines at Bruceton, Pa., which demonstrated that the new Rice barrier and rock dust would prevent an explosion of coal dust from spreading.

The 1915 meeting of the Institute will be held in St. Louis, Mo.  
W. A. HAMOR

## NINTH INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY—ST. PETERSBURG

AUGUST 8-14, 1915

In a letter to Dr. Geo. F. Kunz, dated 2/20/1914, Riga, Prof. Dr. Paul Walden, President of the Ninth International Congress of Applied Chemistry, makes the following announcements:

1—The meetings of the Ninth International Congress of Applied Chemistry will be held in St. Petersburg, August 8-14, 1915.

2—Excursions will be made to Finland, Moscow, Kiew, Baku in the Caucasus, etc.

3—In addition to the usual addresses, systematic reviews of the work in particular fields (with discussions) are to be given by specialists, on the invitation of the Committee of Organization, to a greater extent than formerly.

4—Particulars as to receptions, entertainments, etc., will be given later.

5—The question of reduced railway fares on the Russian railroads is now under consideration by the Government.

6—No obstacles will be placed in the way of the journey of Jewish chemists to the Congress provided that at the frontier, in addition to the viséed passport (requisite for every passenger), cards of membership, signed by the President and Honorary Secretary of the IX International Congress shall have been presented.

7—An announcement of the IX International Congress in English will be expedited in the course of the next few days or weeks to North America and England.

VAN'T HOFF FUND FOR THE ENDOWMENT OF RESEARCH IN PURE AND APPLIED CHEMISTRY—  
COMMUNICATION TO APPLICANTS

In accordance with the regulations of the van't Hoff Fund founded June 28, 1913, applicants for grants are instructed as follows:

The foundation is located at Amsterdam, and is under the supervision of the Royal Academy of Sciences. On March 1st of each year, beginning with 1915, grants will be made to investigators in the field of pure and applied chemistry who have applied for such funds previous to November 1st preceding.

The Committee in charge of awards at present consists of A. F. Holleman, *President*; F. M. Jaeger, *Secretary*; S. Hoogewerf and A. Smits. This committee has power to appoint such assistants, for a term of one year, as they may deem necessary to a proper consideration of the applications.

The names of individuals to whom the grants are made will be published. The grantees are expected to send copies of any publications resulting from their work to the committee. They are at liberty to choose the manner of publication and the journal

in which their results are published, but they are expected to give credit to the van't Hoff Fund.

The amount available for 1915 is about \$320. Applications should be sent by registered post to "Het Bestuur der Koninklijke Akademie van Wetenschappen; bestemd voor de Commissie van het 'van't Hoff-fonds,' Trippenhuis, Kloveniersburgwal, te Amsterdam," with a detailed account of the use to which the grant is to be put, and of the grounds upon which the application is made.

AMSTERDAM  
May, 1914

For the van't Hoff Fund.

A. F. HOLLEMAN, *President*  
F. M. JAEGER, *Secretary*

AMERICAN CHEMICAL SOCIETY—ANNUAL MEETING  
MONTREAL, SEPTEMBER 15-18, 1914

Owing to the Cartier Celebration which takes place in Montreal during the week commencing Sunday, September 6th, it has been found necessary to change the date of the Montreal meeting to September 15th-18th, with the Council Meeting on Monday, September 14th, in the evening.

CHAS. L. PARSONS, *Secretary*

## AMERICAN CHEMICAL SOCIETY DIRECTORY, 1914

The 1914 Directory of the American Chemical Society is about to be issued. Members of the Society can secure copies by request to the Secretary, accompanied by twenty-five cents and the statement that "The Directory will not be loaned or disposed of to any firm or individual for advertising purposes." There are so many firms in the country that are anxious to secure the Directory of the Society to circularize the membership rather than advertise in our Journals that the Directors have deemed it necessary to require this statement before distribution.

CHARLES L. PARSONS, *Secretary*

INDUSTRIAL CHEMISTS AND CHEMICAL ENGINEERS  
DIVISION A. C. S.—COMMITTEE ON ALUM  
SPECIFICATIONS—CORRECTION  
AND NOTICE

In the tentative alum specifications given in THIS JOURNAL, 6, 435, in the second item "Standard Grade," the figure for iron should be "0.50 per cent" instead of "50 per cent" as printed.

The writer wishes to announce that he is prepared to receive and classify methods for the analysis of alum so that they can be presented with the specifications for final action by the Society.

WM. M. BOOTH

DILLAVE BUILDING  
SYRACUSE, NEW YORK  
June 3, 1914

THE DIFFERENTIATION OF NATURAL AND OIL  
ASPHALTS—CORRECTION

In accordance with permission received from the Editor of THIS JOURNAL, we reprinted, in pamphlet form, the article appearing in the April issue, p. 286, under the above title, by E. C. Pailer. In making this reprint, two sentences were italicized; *vis.*, "If the chemist has no means of detection, is it any wonder that the practice of substituting oil asphalt for natural asphalt exists?" and "The process to convert oil into asphalt, which took ages in nature, is used in the manufacture of oil asphalts, and is accomplished in a few days."

We make this acknowledgment in order to correct as far as possible the impression that the sentences referred to were italicized in the original publication.

THE BARBER ASPHALT PAVING COMPANY  
D. G. PIERCE, *Executive Assistant*

LAND TITLE BUILDING  
PHILADELPHIA  
June 3, 1914



## PERSONAL NOTES

The annual meeting of the American Society for Testing Materials will be held in Atlantic City, June 30-July 3, 1915.

Prof. S. F. Acree, of the Department of Chemistry at Johns Hopkins University, Baltimore, has been appointed Chief of the Chemical Division of the Forest Products Laboratory of the Forest Service in cooperation with the University of Wisconsin. Prof. Acree will lecture on celluloses, starches, sugars and other related topics.

Professor George C. Whipple, of Harvard University, has been chosen as one of the three American engineers to act with three Canadian engineers to advise with the International Joint Commission on matters pertaining to the pollution of the Great Lakes.

The annual general meeting of the Society of Chemical Industry will be held in Nottingham, England, on July 15-17, 1914. The Society's Medal will be presented to the Rt. Hon. Sir Henry E. Roscoe, LL.D., F.R.S. Addresses will be made by the President, Dr. Rudolph Messel and by Sir William Crookes, President of the Royal Society.

Dr. Charles H. Kimberly, Professor of Analytical Chemistry at the Medico-Chirurgical College, Philadelphia, since 1907, resigned on June 1st to become a member of the staff of the Bureau of Chemistry, Department of Agriculture, at Washington.

The St. Louis Section of the A. C. S. was addressed on June 8th by Dr. Sidney Born, of the Lemp Brewing Co., on "The Purification and Sterilization of Air Industrially."

Mr. Stephen DeM. Gage has resigned as Biologist at the Lawrence Experiment Station of the Massachusetts State Board of Health, to accept the position of Chemist to the Rhode Island State Board of Health.

Mr. J. Russel Marble, of Worcester, Mass., has been elected President of the New England Section of the North Eastern Section of the A. C. S. On a recent excursion, the Section visited the mills of the Amoskeag Mfg. Co. at Manchester, N. H. Dr. W. K. Robbins, the Superintendent of Coloring, gave a most instructive address on "Science Applied to Industry."

Mr. J. Franklin McKinnell has accepted a position with S. Gompert & Co., Manufacturers of Baker's Specialties, of Brooklyn, as chief chemist and factory superintendent.

The Philadelphia Section of the A. C. S. held its final meeting of the 1913-14 season on the afternoon and evening of June 12th. A factory inspection trip to the plant of the Welsbach Co. at Gloucester, N. J., in the afternoon was followed by a dinner in the evening at the Ridgway Hotel in Camden.

To date the United States Steel Corporation has expended more than \$800,000 in experimental work on the electro-thermal production of steel.

On May 25th, Professor M. A. Rosanoff, of Clark University, addressed the Research Staff of the Mellon Institution, University of Pittsburgh, presenting a theory of the mechanism of sugar inversion by acids.

Dr. Walter F. Rittman has been appointed Oil and Gas Technologist for the U. S. Bureau of Mines. Mr. Rittman's headquarters will be at Pittsburgh.

Dr. L. H. Baekeland leaves July 8th for a trip around the world. He expects to visit and study the chemical industries and developments in Japan, Korea, Manchuria and Mongolia, returning to Europe via the Trans-Siberian Railway.

Miss Jessie Y. Cann, Ph.D. (Columbia), Head of the Department of Chemistry at Rockford College, Rockford, Ill., has accepted an instructorship in chemistry at the University of Illinois.

Mr. Clifford Richardson, consulting engineer, has been elected President of the Association of Harvard Chemists, and Vice-President of the Harvard Engineering Society of New York, for the ensuing year.

The 7th Congress of the International Association for Testing Materials will be held in St. Petersburg, August 12-17, 1915. Arrangements have been made for extensive excursions in the interior of Russia, after the Congress.

The Coal Mining Institute of America held its annual summer meeting in Monongahela, Pa., on June 16th and 17th. The matter of safety protection for miners was the principal subject of discussion.

The Electric Generating Plant built by the Virginian Power Co., recently commenced supplying power to the coal mines in the Kanawha-New River District of W. Va. The plant is located about 15 miles from Charleston, W. Va., on the Kanawha River; its transmission and distribution lines are about 129 miles in length and extend through territory containing over 250 producing coal mines.

Sir Joseph Wilson Swan, known for his important discoveries in connection with the carbon filament lamp, electrochemistry and photography, died on May 27th, in his 86th year.

In its report to Congress, the Commission on Vocational Education has recommended that \$7,000,000 be appropriated annually for the promotion of greater skill in the common occupations. The Commission emphasized the importance of this educational work and asserts, moreover, that it presents the country's greatest need.

Professor John Howard Appleton, for over fifty years an instructor at Brown University and since 1868 head of the Department of Chemistry, will retire at the end of the present academic year with the title of Professor Emeritus.

Thomas Dolan, formerly one of the largest textile manufacturers in Philadelphia, and later interested in street railways, died in Philadelphia on June 12th, aged 82.

Prévost Hubbard, in charge of the Division of Roads and Pavements, The Institute of Industrial Research, Washington, and Arthur H. Blanchard, Professor of Highway Engineering at Columbia University, have been elected by the Council of the International Association of Testing Materials, the American members on a commission on "Standardization of Methods of Testing and Nomenclature of Road and Paving Materials."

The Chemical Products Company, organized in 1902, and now managed by Arthur D. Little, Inc., to develop applications of cellulose acetate, has paid 8 per cent on preferred since its organization, and has recently declared 30 per cent on its common stock. The Mansfield Company, under the same management, is now erecting a plant at Mansfield, Mass., for the manufacture of waterproof paper for case linings.

Professor Edmond O'Neill, Head of the Department of Chemistry of the University of California, attended the recent meeting of the American Institute of Chemical Engineers at Troy and spent the following week in New York visiting friends. While in New York, Prof. O'Neill was registered at the Chemists' Club.

# GOVERNMENT PUBLICATIONS

By R. S. McBRIDE, Bureau of Standards, Washington

**NOTICE**—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate. Consular Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington. The regular subscription rate for these Consular Reports mailed daily is \$2.50 per year, payable in advance, to the Superintendent of Documents.

## DEPARTMENT OF AGRICULTURE

**Reduction of Arsenic Acid to Arsenious Acid by Thiosulfuric Acid.** By ROBERT M. CHAPIN. Reprinted from the *Jour. of Agricultural Research*, 1, 515-7 (1914); but not available as a separate.

**Crystallization of Cream of Tartar in Fruit of Grapes.** By WILLIAM B. ALWOOD. Reprinted from *Jour. of Agricultural Research*, 1, 513-4 (1914); but not available as a separate.

**Monthly Weather Review.** Beginning with January, 1914, the climatological data formerly issued as a part of the monthly weather review will be issued monthly from 44 section centers. The *Monthly Weather Review* and the *Bulletin of Mount Weather Observatory* are to be merged into a single publication having the former title; some articles of chemical and physical interest will now be included. The following titles are examples of these.

**Atmospheric Transparency for Radiation.** By F. E. TOWLE. *Monthly Weather Review*, 42, 2-4 (1914); also available as a separate. This gives "a comparison of the transparency of the earth's atmosphere as determined by different observers at various altitudes with values derived by computation from the barometric height, the amount of aqueous vapor, and the transparency above Mount Wilson for dry air." The effect of scattering due to the molecules of the air itself, water vapor, and dust, is discussed.

**Pressure in Absolute Units.** By W. N. SHAW. *Monthly Weather Review*, 42, 5-7 (1914). A plea for use of metric units and nomenclature in meteorological work.

**The Meteorological Aspect of the Smoke Problem.** By H. H. KIMBALL. *Monthly Weather Review*, 42, 29-35 (1914); also available as a separate, including a list of references. A condensed report with additions and revisions from Smoke Investigation Bulletin 5, Mellon Institute, Univ. of Pittsburgh. The following summary indicates the scope and general conclusions of the work:

"1. City fogs are more persistent than country fogs, principally because of their increased density on account of the smoke that accumulates in them.

"2. In consequence of the above there are fewer hours of sunshine in cities than in the country.

"3. In the clear part of the day in winter in London the average limit of visibility does not exceed one-half mile. In Pittsburgh it averages about 1 1/2 miles. This latter is less than one-tenth the average limit of visibility in the open country about Pittsburgh.

"4. The chemical action of light in smoky cities has been found to be 40 per cent less than in the open country, and over 20 per cent less on smoky days than on comparatively clear days.

"5. Minimum temperatures are markedly higher in cities than in the country, partly on account of city heating, but principally because the smoke acts as a blanket to prevent the escape of heat at night."

**On the Amount of Evaporation.** By Y. HORIGUTI. *Monthly Weather Review*, 42, 101-5 (1914). Revised reprint from *Jour. of the Meteorological Society of Japan*, 32, 14-26 (1913). The rate of evaporation of water exposed to air and sun is studied by experiments and mathematical treatment. The discussion should be of interest in connection with industrial work where solutions must be concentrated. The following factors enter: Humidity of air, air temperature, water temperature, wind velocity, atmospheric pressure, sunshine, boundary conditions, etc.

**Relation of Bacterial Transformations of Soil Nitrogen to Nutrition of Citrus Plants.** By K. F. KELLERMAN and R. C. WRIGHT. *Jour. Agricultural Research*, 2, 100-14. Not yet available as a separate.

**Aroma of Hops; a Study of the Volatile Oil with Relation to the Geographical Sources of the Hop.** By FRANK RABAK, Bureau of Plant Industry. *Jour. Agricultural Research*, 2, 115-59. Available also as a separate. A study has been made of numerous physical and chemical properties of hop oils from various sources and various years, and it is shown that the geographic source of hops may be indicated by the ester numbers of the oil.

**The Topographic Features of the Desert Basins of the United States with Reference to the Possible Occurrence of Potash.** By E. E. FREE. Department Bulletin 54, from the Bureau of Soils. 65 pp. 25c. This paper describes a topographical examination which has been made of the desert basins of the United States, with a view to the possible discovery of potash in commercial quantities, and is intended particularly for those interested in the production of fertilizers.

**Suitability of Longleaf Pine for Paper Pulp.** By HENRY E. SURFACE and ROBERT E. COOPER. Department Bulletin 72, from the Forest Service. 26 pp. 5c. Report of a series of tests in cooperation with the University of Wisconsin, undertaken, (1) to determine the suitability of the southern pines for paper pulps, (2) to ascertain the effects of varying cooking conditions in the sulfate process of pulp making, (3) to compare the sulfate process with the soda process.

## BUREAU OF THE CENSUS

**Textiles.** The textiles section of the 13th census report on manufactures, as given in Vol. 10, has been reprinted as a separate of 171 pages, which is available for free distribution to those specially interested.

## BUREAU OF FOREIGN AND DOMESTIC COMMERCE

**Commerce.** Miscellaneous Series Nos. 14 and 6d are, respectively, an annual review of the Foreign Commerce of the United States for 1913 and an outline of the service maintained for the promotion of commerce by this and other Bureaus of the Government. No. 14 is available in paper for five cents; No. 6d can be had on application to the Bureau.

**Cotton Goods.** Three reports by RALPH M. ODELL, being special agents series Nos. 80, 82, and 83, respectively 91 pp., 35 pp. and 60 pp.; paper, 15c, 10c and 10c. These three reports discuss the cotton goods statistics and markets for the following three districts: (1) British East Africa, Uganda, Zanzibar, and German East Africa; (2) Portuguese East Africa; and (3) South Africa.

## BUREAU OF STANDARDS

**Surface Insulation of Pipes as a Means of Preventing Electrolysis.** By BURTON McCOLLUM and O. S. PETERS. Technologic Paper 13. 44 pp. The experiments reported show that the pipe paints, dips, and wrappings tested were of no practical value in protecting pipes from electrolytic damage

when used in positive areas near the power house; in negative areas they assist by reducing the amount of current picked up by the pipes. The value for prevention of natural soil corrosion is not discussed in this paper. An appendix of the paper includes a report of the experience and opinions of pipe-owning companies with regard to the prevention of electrolysis and soil corrosion by means of insulating coatings.

**Determinations of Carbon in Steel and Iron by the Barium Carbonate Titration Method.** By J. R. CAIN. Technologic Paper 33. 12 pp. See THIS JOURNAL, June, 1914, 465, for very full abstract.

**Determination of Ammonia in Illuminating Gas.** By J. D. EDWARDS. Technologic Paper 34. 23 pp. See THIS JOURNAL, June, 1914, 468, for short report of the results given in this paper.

**The Silver Voltmeter. Part IV. Third Series of Quantitative Experiment and Special Investigations.** By E. B. ROSA, G. W. VINAL and A. S. McDANIEL. Scientific Paper 220. 64 pp. The object of the work reported in this paper was "to carry out a series of experiments on these two forms of voltmeters (porous-cup and Smith forms) that should afford as complete data as possible for formulating specifications, according to which the voltmeter might be used at any time for the measurement of current and (in connection with resistance standards) for checking the constancy of the Weston normal cell. This work consequently included not only a further comparison of these two forms of voltmeters, but also a study of the effects of traces of uncombined acid or of base in the electrolyte, and of variations of other conditions." The voltage of the Weston normal cell is found by use of these voltmeters to be 1.01827 volts at 20°.

**Influence of Atmospheric Conditions in the Testing of Sugars.** By FREDERICK BATES and F. P. PHELPS. Scientific Paper 221. 21 pp. The evaporation of solutions during filtration causes errors due to change in polarization of filtrate; this error may be corrected for by a formula given, or prevented for all ordinary purposes, by covering funnels with a watch glass while filtering the solution.

#### BUREAU OF MINES

**Electric Furnaces for Making Iron and Steel.** By D. A. LYON and R. M. KEENEY. Bulletin 67. 142 pp. This bulletin gives a well-illustrated, historical review of the development of the electric furnaces for iron and steel manufacture, and discusses the problems which remain to be solved in the use of the electric furnace for the smelting of iron ores and the production of pig iron at a profit on a commercial scale. Some results are given from an investigation now in progress that has for its object the "increasing safety, efficiency, and economic development in the metallurgical industries, the application of electricity to various processes, and especially to those in the manufacture of iron and steel."

**A Preliminary Report on Uranium, Radium, and Vanadium.** By R. B. MOORE and K. L. KIRHL. Bulletin 70. 114 pp. This is a revised and enlarged edition (increase of about 20 pages) of the bulletin of the same name and number issued in December, 1913. "This bulletin presents a summary of available information regarding the sources of uranium, radium, and vanadium, the methods used in treating the ores, and the uses of the finished products." Although treating the subject primarily from the economic and conservation standpoints, some valuable chemical analytical methods are given and mineral tables are included, making the bulletin of considerable value to anyone interested in these elements.

**The Flash Point of Oils; Methods and Apparatus for its Determination.** By I. C. ALLEN and A. S. CROSSFIELD. Technical Paper 49, 2nd edition revised. 37 pp. Includes an extended bibliography.

**Relative Effects of Carbon Monoxide on Small Animals.** By G. A. BURRELL, F. M. SEIBERT and J. W. ROBERTSON.

Technical Paper 62. 23 pp. A report of tests of repeated exposure of canaries, mice, sparrows, and other animals to test their value for detection of carbon monoxide in mine air.

**Problems of the Petroleum Industry.** By I. C. ALLEN. Technical Paper 72. 20 pp. Practically only a report of conferences at Pittsburgh, Pa., on August 1 and September 10, 1913, which led to the organization of the American Petroleum Society, and announcement of the constitution of this society.

**Physical and Chemical Properties of the Petroleum of California.** By I. C. ALLEN, W. A. JACOBS, A. S. CROSSFIELD and R. R. MATTHEWS. Technical Paper 74. 37 pp. Results on a large number of oils are given, including data as to: Specific gravity, heating value, flash point, burning point, viscosity, water, sulfur, and percentage of various fractions on distillation.

#### TREASURY DEPARTMENT

**Specifications for Toilet Paper.** Part of directions to bidders for supplying buildings under control of this department. These specifications are one set of the series prepared by the Bureau of Standards for the General Supply Committee to provide for government paper purchases; they should be of interest to those making and testing paper.

**Production of Precious Metals.** Part II of the Annual Report of the Director of the Mint for the year ending June 30, 1913. This includes the results of a joint investigation with the U. S. Geological Survey of the production of gold and silver in this country during 1912. Full foreign statistics and a discussion of them is included. 88 pp. Cloth, 35c.

#### GEOLOGICAL SURVEY

**Mineral Resources of the U. S., 1912. Part I, Metals. Part II, Non-Metals.** 1079 and 1218 pp. In addition to general statistics of mineral production, the following subjects are discussed in Part I, as chapters which have been republished as separates: Iron ore, pig iron, and steel; manganese; precious and related semi-precious metals (4 sections); gold and silver; copper; lead; zinc; mercury; bauxite and aluminum; cobalt; molybdenum; nickel; tantalum; tin, titanium; tungsten; uranium and vanadium; antimony; bismuth; selenium; chrome iron ore; platinum metals; and cadmium.

Part II contains chapters on the following subjects: Coal; coke; fuel briquettes; natural gas; petroleum; peat; cement; clay-working industry; sand and gravel; gypsum; lime; sand-lime brick; slate; stone; abrasives; arsenic; borax; fluorspar and cryolite; phosphate rock; potash salts; salt and bromine; sulfur, pyrite, and sulfuric acid; barytes and strontium; mineral paints; asbestos; asphalt; feldspar and quartz; fuller's earth; gems and precious stones; graphite; magnesite; mica; mineral wastes; talc and soapstone; and gas, coke, tar and ammonia.

**Mineral Resources of the United States, 1913.** Several chapters have already been published from the 1913 issue on the following subjects: Sulfur, pyrite, and sulfuric acid; bauxite and aluminum; chrome iron ore; feldspar; mineral paints; fuller's earth; mica; slate; the cement industry; sand-lime brick; and fuel briquetting.

**Contributions to Economic Geology. Part I. Metals and Non-Metals Except Fuels.** Bulletin 540. 563 pp. Short papers and preliminary reports of considerable economic interest to the chemical industry are assembled in this annual bulletin. The chapters are in some cases available as separates. The principal headings are as follows: Gold and silver; copper; lead and zinc; iron and manganese; aluminum; structural materials, building stone, etc.; phosphate rock; salines; sulfur and pyrite; and numerous miscellaneous subjects. These subjects are treated primarily from a geologic standpoint but in many cases are of chemical interest as bearing upon questions of supply of mineral resources used in the chemical industries.

Part II of this publication is Bulletin 541. Only part of the chapters for it have been issued; among these are separates treating of the following: Lignite fields (separate reprints for



several parts of the country); and analyses of coal samples from various fields in the United States.

**Part I** of the 1913 contributions to economic geology is in preparation and one separate has been issued. This is entitled "Some Cerusite Deposits in Custer County, Colorado."

#### CONSULAR REPORTS, MAY

A new cement works is to be erected in the province of Punjab, India. (P. 639.)

The plantation and wild rubber industry of the Malay peninsula and the Amazon valley are discussed. (P. 646.)

The output of iron ore (containing about 50 per cent iron) from Caen, France, is increasing. (P. 653.)

Natural gas is reported from Danplim, Manitoba. (P. 678.)

A company has been organized to cultivate coconuts in Panama, and to manufacture copra, rope, rugs, etc. (P. 687.)

The pig iron industry of India is flourishing, but the steel manufacture has not yet proved a success. (P. 740.)

The American Steel Company of Cuba is to build an additional factory near Habana. (P. 805.)

A starch factory at Rioja, Cuba is making 37,000 pounds of starch daily from cassava. (P. 805.)

The output of petroleum, iron ore and platinum from Russia has decreased and that of manganese ore has increased. (Pp. 817-22.)

The coal industry of Manchuria is increasing. (P. 846.)

The European conditioning firms have decided to hereafter employ only distilled water in the scouring of silk for testing. (P. 852.)

A new hardening material for the surface of concrete floors contains 95 per cent of iron dust or iron flour. (P. 885.)

The use of fuel oil for operating agricultural tractors in Argentina, is being studied by that government. (P. 895.)

Imports of sodium nitrate into the U. S. from Chili in 1913 amounted to \$20,718,968, which is 25 per cent more than in 1912. (P. 898.)

The vegetable-oil industry of Marseille includes the following oils, viz., peanut, coconut, sesame, linseed, castor, and kapok. The hydrogenation process is soon to be installed. (P. 912.)

The soya bean industry of Manchuria is increasing. (P. 921.)

A government nitrate monopoly has been established in Honduras, to control the importation and manufacture of potassium nitrate. (P. 930.)

The output of chrome-iron ore in the U. S. in 1913 was very small compared with that of New Caledonia, Rhodesia and Russia. Imports into the U. S. in 1913 were nearly twice that of 1911. (P. 935.)

Two companies in Costa Rica are extracting annually \$1,000,000 worth of gold and silver. (P. 939.)

The third French Congress for Refrigeration will be held at Reims in October, 1914. (P. 944.)

The output of aluminum in the U. S. in 1913 was over 72,000,000 pounds. (P. 973.)

An American syndicate is investigating the placer gold deposits of Peru. (P. 988.)

A syndicate has been formed to develop the phosphate deposits at Gamboola, Australia. Adjacent sulfur deposits make the manufacture of superphosphate possible. (P. 1008.)

The cultivation of lac in India is an important industry, a large part of the product being sent to the U. S. (Pp. 1016-7.)

A factory for the production of coconut oil is to be established on Cebu Island in the Philippines, with an output of 75 tons oil per day. (P. 1019.)

The mineral products of Canada include: Copper, gold, iron, lead, nickel, silver, asbestos, coal, gypsum, natural gas, petroleum, salt, cement, ceramics and lime. (P. 1030.)

The Spanish Government is exploring near Jerez, Spain, for petroleum. (P. 1070.)

To prevent falsification as to the grade and purity of tin exported from Hongkong, China, special arrangements have been made by the government analyst of that place. (P. 1114.)

The exportation of impure or adulterated rubber from the Belgian Congo has been prohibited. (P. 1169.)

The production of "butter" from shea nuts is important in British West Africa. The product is used for making artificial butter, and also for soap and candles. (Pp. 1180-3.)

Statistics and information from consular agents regarding exports from various localities to the United States are given in the following references:

Almeria, Spain. Esparto grass. (P. 598.)

Havre, France. Aluminum, antimony, arsenic, carbons, casein, pigments, copper, dyes, glue, glycerine, hides, lead oxide, drugs, oils (linseed, rapeseed, and essential), paper stock, rubber, porcelain, tallow, zinc oxide (p. 625); and flint pebbles. (P. 652.)

Mexico. Cottonseed, copper, lead and gold ores, silver and zinc ores, rubber, graphite, hides, wax, sugar, and petroleum. (Pp. 705-21.)

Columbia. Copal, gold, guano, hides, drugs, platinum, rubber, silver, sugar, and tannic acid. (P. 728.)

Nova Scotia. Fertilizers, gold, grindstones, gypsum, hides, tar oil, whale oil, manganese ore, pulpwood, raw sugar, and tungsten ore. (P. 763.)

Algiers. Esparto grass, iron ore, olive oil, phosphate rock, and zinc ore. (P. 838.)

Burma. Rubies, sapphires, spinels, and jade. (P. 845.)

Lyons, France. Mineral water, photographic supplies, gold, silver, and copper ore, hides, glue, dyestuffs, and argols. (P. 858.)

Valencia, Spain. Iron ore, olive oil, saffron, peanuts, and hides. (P. 908.)

Marseille, France. Aluminum, argols, arsenic, bark, bauxite, cement, drugs, glue, glycerine, hides, ocher, vegetable oils, iron ore, potassium ferrocyanide, rubber, stearin, tin, and zinc oxide. (P. 917.)

Amazon Valley, Brazil. Rubber. (P. 936.)

Dresden, Germany. Drugs and chemicals, essential oils, and scientific instruments. (P. 942.)

Rotterdam, Holland. Acetic, carbolic, formic, phosphoric, and tartaric acids, aluminum, balances, cocoa butter, ferromanganese, fertilizers, glycerine, crude gum, hides, madder, magnesite, oils (citronella, cottonseed, creosote, fusel, and linseed), oleo stearin, paper stock, prussiate of soda, rubber, poppy and rape seeds, tin, wax, and zinc. (P. 963.)

Zurich, Switzerland. Aluminum, chemicals, ferrosilicon, and gelatin. (P. 999.)

Montreal, Canada. Fertilizers, gas liquor, hides, marble, sodium nitrate, creosote oil, and paper stock. (P. 1050.)

Kobe, Japan. Soya-bean oil, camphor, metals, menthol, and wax. (P. 1058.)

Birmingham, England. Chemicals, glass, glue, gunpowder, rubber goods, paint, platinum, iron and steel, varnish, wood pulp, and yarn. (P. 1100.)

Winnipeg, Canada. Pyrite. (P. 1107.)

Durango, Mexico. Arsenious acid, copper, gold, lead, silver, cottonseed, glycerine, hides, and rubber. (P. 1122.)

Reims, France. Antimony, rubber, chloride of lime, prussiate of soda, and tin. (P. 1139.)

Calais and Boulogne, France. Chalk, pitch, potash, and seed oil. (P. 1140.)

Limoges, France. Glue, kaolin, and filter paper. (P. 1145.)

Grenoble, France. Carbon electrodes, emery, hides, ferro alloys, potassium perchlorate, and photographic paper. (P. 1149.)

## BOOK REVIEWS

**Engineering Thermodynamics.** By CHARLES EDWARD LUCKE, Ph.D., Professor of Mechanical Engineering, Columbia University, New York City. New York: McGraw-Hill Book Company. 1912. 9 X 6, 118 and xxiv pp., 323 illustrations, 143 tables. Price, \$8.00.

An examination of this book cannot fail to impress the reader with the thought that this is a great work destined to become the book of reference on this subject.

Since Rankine's time the science of thermodynamics has been highly developed and has become of great importance in the formulation of modern physical chemistry and its correlated branches in engineering. Thermodynamics, *per se*, is not concerned with any physical substance; it is rather a theory of energy in relation to matter. The author's treatment of engineering thermodynamics is based upon the application of the laws of pure thermodynamics, modified by conditions of practice, to guide computation on thermal problems which deal with physical substances under actual conditions of operation.

The scope and treatment of this work is much more extensive than that ordinarily found in books on thermodynamics. Not only is the subject matter more inclusive in that it covers a wide range of topics not usually considered, but the presentation is given in marked detail. This has involved an enormous amount of labor on the part of the author in developing formulas directly applicable to practical conditions—but it is labor which the busy engineer must certainly appreciate.

Dr. Lucke divides the subject into three general parts, the first dealing with the conditions surrounding the doing of work without any consideration of heat changes; the second, heat gains and losses by substances without reference to work involved; and the third, transformation of heat into work or work into heat in conjunction with changes in the condition of substances. The first part applies to the behavior of fluids in the cylinders of compressors and engines. The second part is concerned with the development of heat by combustion, its transmission from place to place and the effect on the physical condition of solids, liquids, and gases with their mixtures, solutions and reactions. The third part is fundamental to the efficient production of power by gases in internal combustion gas engines or compressed-air engines, and by steam or other vapors on steam engines and turbines, and likewise to the production of mechanical refrigeration by ammonia, carbon dioxide and other vapors.

Accordingly, the six chapters of the book treat these three parts in order. The first three chapters deal with work without any particular reference to heat; the second two with heat, without any particular reference to work; while the last is concerned with the relation between heat and work. After establishing in the first chapter the necessary units and basic principles governing work, the second chapter proceeds to the determination of the work done in compressor cylinders; and the third chapter discusses the available work in engine cylinders in terms of all the different variables that may determine the work for given dimensions of cylinder or for given quantities of fluid. The fourth chapter is devoted to the qualitative and quantitative heat content of substances and their physical-chemical state; the fifth relates to heating by combustion and discusses fuels, furnaces, gas-producers and steam boilers. In the final chapter the general relations between heat and work are presented, and the thermal efficiencies of steam, gas, and compressed air engines are deduced. The flow of expansive fluids and the performance of refrigerating systems are also discussed in this chapter.

Throughout the entire work there have been established a series of working formulas derived from a few simple principles and left in such form as to be readily available for numerical

substitution. This permits the solution of problems on engine and compressor horse-power, fluid consumption or capacity, with very little labor or time, although it has required the expansion of the subject over a considerable number of pages of book matter.

A valuable feature of the work consists in the presentation of extensive tables, diagrams and charts to facilitate the solution of numerical problems. There are nearly 150 tables bearing upon every conceivable phase of engineering thermodynamics; these apply to the various kinds of machinery and apparatus used for heating, evaporating, condensing, melting, freezing, gasification and combustion, as well as the fuels used in power production. It is doubtful whether there exists elsewhere such a comprehensive collection of tables on this subject.

While the book appears to be too large for use as a text in the ordinary courses in thermodynamics, it could be used to good advantage in advanced courses. Its comprehensiveness, including as it does the thermodynamic relations in all forms of heat changing machinery, makes the book particularly valuable as a work of reference on gas power, compressed air, steam turbines, steam power plants, steam engine design, mechanical refrigeration and heating and ventilating. In addition to its use in the class-room and laboratory, it should have a large field of usefulness among practising engineers whether they be engaged in the chemical industries, gas engineering or mechanical engineering.

It is to be regretted that in a work of such magnitude the author has not given complete references to the various sources of information and tabular data. References always enhance the value of any publication and would make still more valuable such an excellent treatise as Dr. Lucke's "Engineering Thermodynamics."

JOHN J. FLATHER

**Das Lebensmittelgewerbe.** By K. VON BUCHKA. Akademische Verlagsgesellschaft. Leipzig, 1913.

The first two parts of this book on foods and condiments contain an introduction on nutrition by A. Kreutz, a general discussion by the editor, von Buchka, and a chapter on coffee by A. Hasterlik.

If the rest of the book is as complete in detail as the opening chapters, it should prove very useful to the food chemist.

SIDNEY BORN

**Exercises in Gas Analysis.** By DR. H. FRANZEN, Professor in Heidelberg; translated by DR. T. CALLAN, Paisley Technical College. Blackie and Son, London. D. Van Nostrand, New York. Pp. 120. Price, \$1.00.

This little book gives a description for the purposes of instruction of the usual methods of analyzing gases by the Hempel, Buntz, and Orsat apparatus. Winkler's dissolved oxygen method and Lunge's nitrometer are also included. The descriptions are very full—too full it would seem in some cases. For example, it would seem to be axiomatic that carbon dioxide would be dissolved by water unsaturated by it, without requiring an experiment (No. 5) to prove it. All the calculations involved in the analytical operations are thoroughly and carefully explained. No attention, however, is paid to the calculations involved in the practical applications of the art, particularly to chimney gases. As the book makes no pretense of being compendious, all references to the literature are omitted. Owing also to the omission of an index, the use of the book is rendered more difficult. The very full Table of Contents does not supply this deficiency.

While in general the directions are very full, yet they lack in

not specifying the precautions to be used in making a gas explosion, both in protecting the operator from bodily injury and in preventing the burning of the nitrogen. No mention is made of the fact that pyrogallol may, unless properly prepared, give off carbonic oxide. An iron tube is used for sampling chimney gases and no statement is made regarding the liability of the carbon monoxide which may be contained in them to be changed to carbon dioxide by the rust upon the tube.

The book is one which cannot fail to be helpful and instructive to the teacher, but owing to omissions such as noted, cannot be unreservedly recommended to the unaided student, nor as a text book to be followed implicitly.

A. H. GILL

**Treatise on the Ceramic Industries: Vol. I, Quantitative Inorganic Analysis.** By J. W. MELLOR, D.Sc., first edition. Charles Griffin and Company, Limited, London. 778 pp., 208 illustrations, 1913. Price, \$7.50.

This imposing volume from the hand of a well-known writer offers to the reviewer a task of considerable magnitude, owing to its wide scope. For this reason the text was discussed with several experienced analysts. The writer is especially indebted to his colleague, Mr. P. H. Bates, for help in reviewing this mass of material. The volume is divided into five parts. Part I describes general analytical processes; Part II deals with the analysis of a simple silicate; Part III suggests methods of dealing with more complex silicates; Part IV discusses modifications necessary in the presence of the more difficult of the rarer elements; Part V refers to the determination of the acid constituents and contains a chapter on the mineral analysis of clays.

The book differs radically and favorably from the typical European treatise on the subject and it is pleasant to read the emphasized acknowledgment of the fundamental work of Dr. Hillebrand. The author has studied and read widely and has been eminently successful in presenting the best methods graded as to accuracy and obtained from many sources. This judicious, broad selection is remarkably complete and includes practically all of the best American processes of analysis.

The reasons for doing things and the statements concerning the conditions under which certain reactions are effective as a means of separation are presented in precise and interesting language. The foot-note references to the literature are probably the most complete that have ever been offered in a book of this character. Attention is called to many details, corrections and to apparatus not commonly described.

The analysis of such silicates as clay is discussed in great detail for every constituent and goes into every refinement. The sources of error are clearly indicated. This chapter is followed by one dealing with rapid work methods. Chapter XIX on electro-analysis is brief but satisfactory. In Chapter XX the author boldly attacks the subject of glaze, glass and enamel analysis, one in regard to which chemical literature has been sadly deficient, owing principally to the limited experience of chemists with this difficult field. Here again he has succeeded in presenting methods for overcoming the principal difficulties which are met. Gravimetric and volumetric procedures are described which include methods for arsenic, antimony, tin, lead, zinc, bismuth, mercury, cadmium, copper, manganese, cobalt and nickel.

The part devoted to special methods treats of the determination of molybdenum, tungsten, niobium, tantalum, gold, platinum, selenium, aluminum and beryllium. Rapid methods are described for the estimation of iron, covering all possible cases. Due attention is given also to the methods of determining chromium, vanadium, uranium, and to such cases as the simultaneous determination of small amounts of titanium and vanadium. These are followed by the treatment of zirconium, thorium and the rare earths. Among the special methods for barium,

strontium, calcium and magnesium, those given for free lime in mortars, etc., might have made mention of the qualitative White microscopic phenol method as being the only satisfactory test for small quantities of free lime. The next chapters are concerned with the special methods for the determination of the alkalies, carbon, carbon dioxide, water, boron, phosphorus, sulfur, fluorine, chlorine and iodine. The last chapter offers a résumé of the mineral analysis of clays, which is very complete. On pages 666-7 numerical errors have crept into the example of a rational analysis calculation.

Dr. Mellor's book is an important contribution to chemical literature. It should prove to be of great value not only to silicate chemists, but to every one engaged in inorganic analysis. It is a remarkably well done summary of our present knowledge relating to analytical methods.

A. V. BLEININGER

**Untersuchung der Kohlenwasserstoffe und Fette.** By D. HOLDE. Berlin: Julius Springer, 1913. 8vo., 612 pages. Price, \$4.50.

This work is the fourth and enlarged edition of "Untersuchung der Minerale und Fette" published in 1909.

A great deal of new material has been added, bringing the work up to date insofar as the available literature is concerned. The greater part of the book is devoted to the methods used in the examination of hydrocarbon oils, which are clearly described and well illustrated by numerous cuts and tables.

Holde has brought together a great deal of valuable data, which should be an excellent reference on the subject.

Many of the methods given are in general use in this country, although the book cannot be taken as a text on industrial practice here.

THOS. T. GRAY

**Coal Tar Distillation.** By ARTHUR R. WARNES. New York: D. Van Nostrand Company; London: John Allan & Company. 185 pages, illustrated. Price, \$2.50.

This work is a concise description of work practice and construction of apparatus used in coal tar distillation in England. In general, the author has confined himself to single preferred methods throughout the work, which methods, as stated in the preface, are those with which he is familiar. The book is happily free from attempts to collate all the information ever published on the particular subject without regard to authenticity or practicability. It will be interesting reading for chemists in general, as well as for those particularly interested in the industry treated.

After a very brief consideration of the nature of coal tar, its transportation from gas works and storage in tar works, the author devotes Chapters III-V, inclusive, to a description of the stills, settings, condensers and coolers used in tar distillation, confining himself to the vertical type of still, which is in use mostly in England. No descriptions are given of the horizontal tar stills, which are in general use in the United States. It may be noted, however, that the largest still described has a capacity of thirty tons, with a fifteen ton still-preferred, while practice in this country is, as a rule, on a basis of about fifty per cent greater capacity than the maximum figure referred to above. The author gives in minute detail the construction of manhole plates, safety valves, and other accessories of the tar still. Following the rather complete description of the apparatus is a brief chapter dealing with the actual distillation process. In Chapters VII and VIII is a very good description of plant and process for working up crude carbolic and cresylic acids. The further working to refined phenol and cresol has been purposely omitted.

The chapters dealing with benzols, naphthas, etc., are clear and concise, and the information given in these does not vary



essentially from United States practice. As practically no pyridine bases are now manufactured in this country, no comment on the portion of the book dealing with this subject can be made. The chapters on crude naphthalene, anthracene, pitch and creosote oil are very brief, and are treated with much less detail than the previous portion of the work would lead one to hope.

In the last chapter of the book on tarworks' tests, the author departs from his custom and gives us an insight into the United States as well as English laboratory methods. The author does not express preferences for any particular method when two or more are given, but seems to feel that the unification and standardization of the methods used in England by different workers are more important than any particular method.

The book is well indexed, the print and paper are good, and the illustrations clear-cut and distinct.

JOHN MORRIS WEISS

**Taschenbuch für die anorganisch-chemische Grossindustrie.**

By LUNGE AND BERL. 5th edition. 305 pp. Julius Springer, Berlin. 1914. Price, \$2.00.

The authors have brought the fifth edition of this valuable pocketbook up to date, and have added only tried and accepted quantitative methods, physical-chemical tables and other data. The book is divided into two parts. The general part, covering 118 pages, includes tables of molecular weights, factors, solubilities, specific weights, temperature scales, melting and boiling points, volume changes, mathematical data, systems of measurement, and a section on patent regulations of various countries. The special part (178 pages) is divided into seventeen sections: fuels and steam boilers; sulfuric acid; hydrochloric acid; bleaching powder; soda (Le Blanc, Solvay and Electrolytic); sulfur recovery; nitric acid; potassium industries; ammonia; illuminating gas; calcium carbide and acetylene; fertilizers; alumina products; cement; preparation of normal solutions; sampling; comparative hydrometer tables. Under each industry the generally used analytical methods and tables are given, both for raw materials and finished products. The book is well printed and well bound, and is a real pocketbook which should prove of considerable value to many industrial chemists and students.

R. K. MURPHY

**Details of Cyanide Practice.** By HERBERT A. MEGRAW. First edition. Size  $6\frac{1}{2} \times 9\frac{1}{2}$  inches. 215 pages, 19 chapters and index. 53 illustrations of the best known cyanide plants in the United States and Canada. Published by the McGraw-Hill Book Company, Inc., New York. 1914. Price, \$2.00 net.

The author, a member of the editorial staff of the "*Engineering and Mining Journal*," made an investigative tour of the principal cyanide mills of North America and published a series of articles on the plants visited. The preface states that "Actual description has been considered of less importance than discussion and correlation of facts gathered from widely different places, the intention having been to present facts and personal opinions, clearly indicated as such, in a form calculated to inform the profession in general and to promote discussion respecting details involving diverging practice." The book is quite a departure from those published previously on the subject of cyaniding gold and silver ores, in that it does not contain past practice or history, but gives in a concise form the present-day practice of the largest cyanide mills in North America. For this reason the book will be appreciated by the man in practice, even though it is not suited as a text-book for technical schools.

The first three chapters, pages 1 to 27 inclusive, describe in detail the treatment of high-grade silver ores of the Cobalt District of Ontario, Canada. Formerly, these ores were smelted with lead ores, but on account of the high smelting charges and

the accumulation of large amounts of speiss at the smelteries, the application of the cyanide process was encouraged. The articles which constitute these three chapters give detailed descriptions of the methods as applied to the treatment of the Cobalt District silver ores.

Chapters IV and V, pages 28 to 49, give the methods used for treating gold ores of the Porcupine district, Ontario, Canada, at the Hollinger Mill and the Dome Mill.

Chapter VI, pages 50 to 66, is devoted to the practice of cyaniding the low-grade gold ores of the Black Hills, South Dakota, which contain from 6 to 8 per cent. of disseminated pyrite and a small amount of telluride. On account of difficulty in treating this character of ore, the practice has been changed in some details from time to time. The author renders service to the cyanide men of other districts in giving this information.

Chapters VII, VIII and IX, pages 67 to 101, contain descriptions of the methods of treating the gold-silver ores of Telluride and of Cripple Creek, Colorado. Comparative costs of the different methods of treatment are given, and also discussion of the original articles which appeared in the *Engineering and Mining Journal*.

Chapters X, XI, and XII, pages 102 to 152, comprise the practice at Tonapah, Nevada, giving flow sheets of the different mills, descriptions of the apparatus used, costs of the operations, and discussions by leading cyanide men on the original articles which appeared in the *Engineering and Mining Journal*.

Chapters XIII and XIV, pages 153 to 167, include the methods of treatment of the varied silver ores of Fairview and Wonder, Nevada, giving costs of the treatments, flow sheets, descriptions of the apparatus, and comparison of stamp and Chilean mill crushing.

Chapter XV, pages 168 to 176, is a description of the practice followed at Republic, Washington, for rebellious gold-silver ores.

Chapters XVI and XVII, pages 177 to 194, describe the cyaniding of gold and gold-silver ores at Grass Valley, and at Soulsbyville, California. The treatments are described in detail, including flow sheets, consumption of chemicals, costs, and illustrations of the plants.

Chapters XVIII and XIX, pages 195 to 211, are on the mills of Arizona, describing the treatment of the gold ores of Kingman, Oatman, and Wickenburg.

The book should be well received by cyanide mill men, as it contains in concise and convenient form the detailed description of the cyaniding of all of the typical gold and silver ores of North America. However, it is not a suitable text for the technical student, as it does not embody the principles of cyaniding.

EDWARD F. KERN

**Taschenbuch für Gerberei-Chemiker.** By H. R. PROCTOR, with the collaboration of E. STASNY and H. BRUMWELL. Translated from the English by J. GETTMAR. Published, Dresden, by J. Steinkopff. 1914. 242 pages. Price, \$1.25.

The object of this handbook is not to replace the author's "*Leather Industries Laboratory Book of Analytical and Experimental Methods*," but to contain in short concise form the analytical methods required by the tannery chemist or leather manufacturer.

The second revised, enlarged edition of the *Leather Industries Laboratory Book* appeared in 1908; since then newer and better methods for raw materials, factory control, leather, etc., have appeared, which are included in the *Pocket Handbook*.

The book is very well arranged, giving the best analytical methods, explaining the essential chemistry involved and giving details as to the manipulation and interpretation of results.

The author has succeeded in producing a handbook which upholds the excellent standard of his larger volume and the value of which will be appreciated both by the tannery chemist and leather manufacturer.

O. KRESS

# NEW PUBLICATIONS

By D. D. BIKOLZHEIMER, Librarian The Chemists' Club, New York

- Asphalts, Natural and Artificial, The Chemistry and Technology of the.** By KOHLER and EDMUND GRAEPE. 2nd ed. L. 8vo. 504 pp. Price, \$4.75. Friedrich Vieweg & Sohn, Brunswick. (German.)
- Cement, Portland, Manufacture.** By C. NASKE. 3rd ed. Lex. 8vo. 496 pp. Price, \$6.00. Th. Thomas, Leipzig. (German.)
- Chemical Industry of Germany 1888 to 1913.** By B. LEPSIUS. 8vo. 107 pp. G. Sulke, Berlin. (German.)
- Clay and Pottery Industries.** By J. W. MELLOR. Demy. 8vo. Price, \$3.75. Charles Griffin & Co., London.
- Dyestuff Chemistry, Textbook of.** By HANS T. BUCHERER. 8vo. Price, \$5.50. Otto Spamer, Leipzig. (German.)
- Electrochemistry, Principles and Applications of, Vol. IV.** By O. DONY-HENAUT, H. GALL and P. A. GUYE. 8vo. 183 pp. Price, \$6.00. Ch. Béranger, Paris. (French.)
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## RECENT JOURNAL ARTICLES

# RECENT INVENTIONS

By C. L. PARKER, Solicitor of Chemical Patents, McGill Building, Washington, D. C.

**Substitute for Vulcanite.** E. Knoll, March 3, 1914. U. S. Pat. 1,088,907. A gelatinous mass is first produced by boiling ground rubber refuse with oil. This is mixed with powdered slate, oil, and sulfur and the mixture vulcanized. The vulcanized product is then mixed with a caoutchouc substitute, oil and sulfur, the amount of rubber being not materially above 2 per cent of the entire mass, and the resulting mixture is vulcanized.

**Metallurgical Method.** H. Kuzel, March 3, 1914. U. S. Pat. 1,088,909. Refractory metallic oxides such as zirconium oxides are reduced by the action of metallic calcium in an inert environment.

**Vegetable Glue.** F. Lehmann and J. Stocker, March 3, 1914. U. S. Pat. 1,089,064. Seaweed is boiled in water and the solution filtered. Dilute acid and an astringent are then added to the solution and the mass heated for a prolonged period.

**Synthetic Preparation of Ammonia from Its Constituents.** A. Matignon, March 3, 1914. U. S. Pat. 1,089,241. A nitrogen and hydrogen mixture under pressure is passed over finely divided tungsten powder spread upon an asbestos support.

**Bleaching Fats and Oils.** F. Mueller, March 3, 1914. U. S. Pat. 1,089,253. The fats and oils are treated with an alkaline solution of sodium hydrosulfite.

**Treating Petroleum Oils with Ultra-Violet Light.** C. Ellis, March 3, 1914. U. S. Pat. 1,089,359. Oils containing gum-forming components are subjected to the action of ultra-violet light; the gum-forming agents become polymerized and the treated oils become adapted for use as lubricants.

**Refractory Zinc-Lead Ores.** P. C. C. Isherwood, March 10, 1914. U. S. Pat. 1,089,412. Zinc is recovered from prepared refractory zinc-lead ore by heating it under basic conditions with a quantity of fresh sulfuric acid less than that necessary to completely dissolve the zinc contained in the ore and producing a highly basic solution of zinc. The partially extracted ore is then leached under conditions of high temperature and pressure.

**Distilling Crude Pyroligneous Acid.** M. Klar, March 10, 1914. U. S. Pat. 1,089,417. Crude pyroligneous acid is heated to a relatively high, tar-forming temperature in a pre-heater. The precipitate formed by so heating the crude acid is removed and the purified acid distilled at a lower temperature.

**Tungsten Manufacture.** T. W. Frech, Jr., March 10, 1914. U. S. Pat. 1,089,757. Oxid of tungsten for subsequent reduction to tungsten and the drawing of such tungsten into incandescent lamp filaments is produced by heating tungsten-bearing material with a relatively small amount of a compound of thorium under oxidizing conditions.

**Decolorizing Glycerin.** F. Lindner, March 10, 1914. U. S. Pat. 1,089,775. The glycerin is decolorized by the action of a formaldehyde sulfoxylate.

**Hydrating Phosphorus Pentoxid.** S. Peacock, March 10, 1914. U. S. Pat. 1,089,784. Phosphorus pentoxid is subjected to the action of water at a temperature above 900° C. until sufficient phosphoric acid is formed to produce a solution of substantially 1.2 Baumé and then maintaining the temperature of the material above 1000° C. but below its boiling point for a prolonged period.

**Saccharometer.** A. Eppens, March 10, 1914. U. S. Pat. 1,089,464. In this apparatus the measuring liquid is contained

in a measuring tube, *a*, in the rear of which a graduation may be provided. Against the space *b*, in which the urine sugar is subjected to fermentation, the tube *a* is closed by a seal, *c*, which is impermeable to the measuring liquid but is permeable to the carbonic acid produced by the fermentation, thus preventing the measuring liquid from coming into any contact with the urine or the fermentation agent. The measuring tube is likewise closed by a similar seal, *d*, so that the apparatus may be carried about without allowing the measuring liquid to run out. The space *b* is closed by a plug, *f*, and a packing, *g*. By means of a screw, *e*, acting on the plug the level of the measuring liquid can always be set at zero with great precision. The effects in the apparatus caused by the glycogen of the fermentation substance contained in a glass, *i*, are equalized by the provision above the measuring liquid of a second fermentation chamber, *h*, charged for the measuring operation with the same quantity of fermenting substance likewise in a glass, *k*, and the same quantity of liquid as the chamber *b*, the liquid chosen being preferably water. The quantity of carbonic acid generated in the chamber *h* is thus equal to that produced in chamber *b* by the glycogen in the fermenting medium and their actions on the measuring liquid are therefore equalized.

**Titanium and Other Alloys.** E. Kraus, March 10, 1914. U. S. Pat. 1,089,773. Oxid of titanium is fused and aluminum is introduced into the fused mass, the titanium is reduced to the metallic state and caused to unite with the aluminum in the form of an ingot.

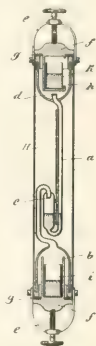
**Adhesive Material for Gluing.** F. Rampichini, March 10, 1914. U. S. Pat. 1,089,960. The adhesive consists of celluloid combined with a suitable solvent and oxalic acid.

**Making Alumina.** H. T. Kalmus and W. L. Savell, March 17, 1914. U. S. Pat. 1,090,479. Sulfitable aluminous material is subjected to a sulfiting operation by the action of sulfur dioxide and water to transform the alumina content of the material into a relatively unstable soluble compound of alumina and sulfur dioxide. The solution is desulfited to break down the unstable compound of alumina and sulfur dioxide and to thus precipitate alumina from the solution.

**Borax and Boric Acid.** E. L. Fleming, March 17, 1914. U. S. Pat. 1,090,526. Borax, boric acid, and sodium chlorate are produced by reacting upon a borate of an alkaline earth metal with a solution of a carbonate and separating a fraction of the borax from the resulting solution by crystallization. The mother liquor which still contains borax is concentrated to produce a hot concentrated solution of borax. On treating with chlorine gas, boric acid and sodium chlorate are crystallized from the solution.

**Separating Mixtures of Gases.** A. Sinding-Larsen, March 24, 1914. U. S. Pat. 1,091,023. This process of separating gases is based upon the property of hemoglobin, as for instance blood, and other similar substances of absorbing various gases and giving them off when physical conditions are changed.

Gas mixtures to be separated are brought into contact with a solution containing hemoglobin in an absorption chamber. The resulting solution is then subjected to fractional evacuation to successively separate the different oxygen-containing gases contained in the hemoglobin.





# MARKET REPORT

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR THE MONTH OF JUNE, 1914

## ORGANIC CHEMICALS

Acetanilid.....	Lb.	21 1/2	@	22
Acetic Acid (28 per cent).....	C.	1.50	@	1.65
Acetone (drums).....	Lb.	10 1/2	@	11
Alcohol, denatured (180 proof).....	Gal.	33	@	35
Alcohol, grain (188 proof).....	Gal.	2.52	@	2.54
Alcohol, wood (95 per cent).....	Gal.	1.50	@	1.55
Amyl Acetate.....	Gal.	1.50	@	1.55
Aniline Oil.....	Lb.	10 1/2	@	10 1/2
Benzoic Acid.....	Lb.	23	@	27
Benzol (90 per cent).....	Gal.	23	@	25
Camphor (refined in bulk).....	Lb.	23	@	25
Carbolic Acid (drums).....	Lb.	7 1/2	@	44 1/2
Carbon Bisulfide.....	Lb.	7 1/2	@	9
Carbon Tetrachloride (drums).....	Lb.	6 1/2	@	8
Chloroform.....	Lb.	77 1/2	@	72 1/2
Citric Acid (domestic), crystals.....	Lb.	19	@	24
Dextrine (corn).....	C.	63	@	—
Dextrine (imported potato).....	Lb.	2.87	@	3.12
Ether (U. S. P., 1900).....	Lb.	48 1/4	@	5
Formaldehyde.....	Lb.	18	@	24
Glycerine (dynamite).....	Lb.	81 1/2	@	91 1/2
Oxalic Acid.....	Lb.	191 1/4	@	191 1/2
Pyrogallol Acid (bulk).....	Lb.	71 1/2	@	79 1/2
Salicylic Acid.....	Lb.	1.20	@	1.40
Starch (cassava).....	Lb.	25	@	27
Starch (corn).....	Lb.	31 1/4	@	4
Starch (potato).....	C.	2.09	@	2.20
Starch (rice).....	Lb.	4	@	41 1/4
Starch (sago).....	Lb.	7	@	8
Starch (wheat).....	Lb.	21 1/4	@	28 1/4
Tannic Acid (commercial).....	Lb.	49 1/4	@	51 1/4
Tartaric Acid, crystals.....	Lb.	33	@	36
	Lb.	30	@	30 1/2

## INORGANIC CHEMICALS

Acetate of Lead (brown, broken).....	Lb.	71 1/4	@	71 1/2
Acetate of Lime (gray).....	C.	1.50	@	1.55
Alum (lump).....	C.	1.75	@	2.00
Aluminum Sulfate (high-grade).....	C.	1.25	@	1.75
Ammonium Carbonate, domestic.....	Lb.	8	@	8 1/2
Ammonium Chloride, gray.....	Lb.	51 1/4	@	61 1/2
Aqua Ammonia (drums) 16°.....	Lb.	21 1/4	@	21 1/4
Arsenic, white.....	Lb.	3	@	31 1/4
Barium Chloride.....	Lb.	19 1/4	@	19 1/4
Barium Nitrate.....	Lb.	5	@	5 1/4
Barytes (prime white, foreign).....	Ton	19.00	@	23.50
Bleaching Powder (35 per cent).....	C.	1.20	@	1.25
Blue Vitriol.....	C.	4.65	@	5.25
Borax, crystals (bags).....	Lb.	33 1/4	@	41 1/2
Boric Acid, crystals (powd.).....	Lb.	7 1/2	@	8
Brimstone (crude, domestic).....	Ton	22.00	@	22.50
Bromine, bulk.....	Lb.	30	@	35
Calcium Chloride, fused.....	C.	60	@	65
Chalk (light precipitated).....	Lb.	4	@	41 1/2
China Clay (imported).....	Ton	14.00	@	16.00
Feldspar.....	Ton	8.00	@	12.00
Fuller's Earth, powdered, Foreign.....	Ton	16.00	@	17.00
Green Vitriol (bulk).....	C.	55	@	60
Hydrochloric Acid (18°).....	C.	1.15	@	1.65
Iodine (resublimed).....	Lb.	3.55	@	3.60
Lead Nitrate.....	Lb.	8	@	8 1/4
Litharge (American).....	Lb.	5 1/2	@	5 1/4
Lithium Carbonate.....	Lb.	65	@	70
Magnesium Carbonate.....	Lb.	21	@	35
Magnesian "Calcedin".....	Ton	28.50	@	29.50
Nitric Acid, 36°.....	Lb.	37 1/2	@	41 1/4
Phosphoric Acid (sp. gr. 1.75).....	Lb.	20	@	24
Phosphorus.....	Lb.	45	@	1.00
Plaster of Paris.....	Bbl.	1.50	@	1.70
Potassium Bichromate, 50°.....	Lb.	61	@	7
Potassium Bromide.....	Lb.	39	@	40
Potassium Carbonate (calcedin), 80 @ 85°.....	C.	7 1/2	@	31 1/2
Potassium Chlorate, crystals.....	Lb.	7 1/4	@	79 1/4
Potassium Cyanide (bulk), 98-99%.....	Lb.	19	@	22
Potassium Hydroxide.....	C.	4.35	@	6.00
Potassium Iodide (bulk).....	Lb.	2.95	@	3.00
Potassium Nitrate (crude).....	Lb.	49	@	51 1/4
Potassium Permanganate (bulk).....	Lb.	92	@	10
Quicksilver, Flask (75 lbs.).....	37.00	@	37.50	
Red Lead (American).....	Lb.	6	@	6 1/4
Salt Cake (glass makers).....	C.	55	@	65

Silver Nitrate.....	Oz.	36 1/4	@	37
Soapstone in bags.....	Ton	10.00	@	12.00
Soda Ash (48 per cent).....	C.	67 1/2	@	72 1/4
Sodium Acetate.....	Lb.	34 1/4	@	41 1/4
Sodium Bicarbonate (domestic).....	C.	1.00	@	1.10
Sodium Bicarbonate (English).....	Lb.	24 1/4	@	3
Sodium Bichromate.....	Lb.	44 1/4	@	5
Sodium Carbonate (dry).....	C.	60	@	80
Sodium Chlorate.....	Lb.	74 1/4	@	71 1/4
Sodium Hyposulfite, 60 per cent.....	C.	1.55	@	1.57 1/2
Sodium Hydrosulfite.....	C.	1.30	@	1.60
Sodium Nitrate, 95 per cent, spot.....	C.	2.12 1/2	@	2.15
Sodium Silicate (liquid).....	C.	65	@	1.50
Strontium Nitrate.....	Lb.	64 1/4	@	7
Sulfur, Flowers (sublimed).....	C.	2.20	@	2.60
Sulfur, Roll.....	C.	1.85	@	2.15
Sulfuric Acid, 60° B.....	C.	85	@	1.00
Talc (American).....	Ton	15.00	@	20.00
Terra Alba (American), No. 1.....	C.	75	@	80
Tin Bichloride (50°).....	Lb.	111 1/4	@	12 1/2
Tin Oxide.....	Lb.	36	@	38
White Lead (American, dry).....	Lb.	54 1/4	@	54 1/2
Zinc Carbonate.....	Lb.	81 1/2	@	9
Zinc Chloride (granulated).....	Lb.	44 1/4	@	5
Zinc Oxide (American process).....	Lb.	54 1/4	@	64 1/4
Zinc Sulfate.....	C.	2.35	@	2.70

## OILS, WAXES, ETC.

Beeswax (pure white).....	Lb.	45	@	47
Black Mineral Oil, 29 gravity.....	Gal.	134 1/2	@	14
Castor Oil (No. 3).....	Lb.	8	@	8 1/4
Ceresin (yellow).....	Lb.	12	@	22
Corn Oil.....	C.	6.45	@	6.50
Cottonseed Oil (crude), f. o. b. mill.....	Gal.	47 1/2	@	47 1/2
Cottonseed Oil (p. s. y.).....	Lb.	7.20	@	7.25
Cylinder Oil (light, filtered).....	Gal.	24 1/2	@	32
Japan Wax.....	Lb.	12	@	13
Lard Oil (prime winter).....	Gal.	92	@	95
Linseed Oil (raw).....	Gal.	51	@	—
Menhaden Oil (crude).....	Gal.	nominal	@	—
Neatsfoot Oil (20°).....	Gal.	96	@	98
Paraffine (crude, 120 & 122 m. p.).....	Lb.	3 1/4	@	3 1/4
Paraffine Oil (high viscosity).....	Gal.	27	@	28
Rosin ("F" grade) (280 lbs.).....	Bbl.	4.50	@	—
Rosin Oil (first run).....	Gal.	—	@	27
Shellac, T. N.....	Lb.	15	@	16
Spermaceti (cake).....	Lb.	30	@	31
Sperm Oil (bleached winter), 38°.....	Gal.	70	@	71
Spindle Oil, No. 200.....	Gal.	18	@	19
Stearic Acid (double-pressed).....	Lb.	84 1/4	@	9
Tallow (acidless).....	Gal.	65	@	66
Tar Oil (distilled).....	Gal.	30	@	31
Turpentine (spirits of).....	Gal.	49	@	49 1/2

## METALS

Aluminum (No. 1 ingots).....	Lb.	17	@	18
Antimony (Hallet's).....	Lb.	64 1/4	@	71 1/4
Bismuth (New York).....	Lb.	2.05	@	2.10
Bronze powder.....	Lb.	50	@	3.00
Copper (electrolytic).....	Lb.	134 1/4	@	134 1/4
Copper (lake).....	Lb.	137 1/4	@	14
Lead, N. Y.....	C.	3.90	@	—
Nickel.....	Lb.	50	@	55
Platinum (refined).....	Oz.	43.50	@	44.50
Silver.....	Oz.	56 1/4	@	—
Tin.....	C.	30	@	60
Zinc.....	C.	5.10	@	5.15

## FERTILIZER MATERIALS

Ammonium Sulfate.....	C.	2.57 1/2	@	2.60
Blood, dried.....	Unit	3.25	@	—
Bone, 4 1/2 and 50, ground, raw.....	Ton	30.00	@	—
Calcium Cyanamid.....	C.	2.20	@	2.25
Calcium Nitrate (Norwegian).....	C.	2.05	@	2.15
Castor meal.....	Unit	3.25	@	—
Fish Scap, domestic, dried.....	Unit	3.25	@	10
Phosphate, acid, 16 per cent bulk.....	Ton	7.00	@	—
Phosphate rock; f. o. b. mine:				
Florida land pebble, 68 per cent.....	Ton	2.25	@	2.50
Tennessee, 70-80 per cent.....	Ton	5.00	@	5.50
Potassium, "muriate," basis 80 per cent.....	Ton	39.07	@	—
Pyrites, furnace size, imported.....	Unit	0.131 1/4	@	—
Tankage, high-grade.....	Unit	3.25	@	—

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## TABLE OF CONTENTS

### EDITORIALS:

The Future of Scientific Research..... 618

### ORIGINAL PAPERS:

Ozone in Ventilation. By J. C. Olsen and Wm. H. Ulrich..... 619

The Fluorescence of Petroleum Distillates. By Benjamin T. Brooks and Raymond F. Bacon..... 623

The Manufacture of Ethyl Alcohol from Wood Waste—Preliminary Experiments on the Hydrolysis of White Spruce. By F. W. Kressmann..... 625

The Oil of Port Orford Cedar Wood and Some Observations on *d-α*-Pinene. By A. W. Schorger..... 631

The Relation between Aluminum Sulfate and Color in Mechanical Filtration. By Frank E. Hale..... 632

Some Further Results of the Hypochlorite Disinfection of the Baltimore City Water Supplies—A Comparison of the Reduction of the Different Members of the *B. Coli* Group. By J. Bosley Thomas and Edgar A. Sandman..... 637

A Sanitary Survey of White River. By John C. Diggs..... 639

An Investigation into the Chemistry of Laundering. By W. F. Faragher..... 640

A Practical Method for the Preparation of Dry Starch, Soluble in Cold Water, for Use as an Indicator. By Robert M. Chapin..... 649

Determination of Silver and Base Metal in Precious Metal Bullion. By Frederic P. Dewey..... 650

The Determination of Chromium and Manganese in Iron and Steel. By Fred C. T. Daniels..... 658

Printing Inks and Their Analysis. By J. B. Tuttle and W. H. Smith..... 659

The Occurrence of Manganese in Kentucky Soils and Its Possible Significance. By O. M. Shedd..... 660

On the Composition and Value of Bat Guano. By C. F. Miller..... 664

Studies in Synthetic Drug Analysis—I. Estimation of Acetanilide and Phenacetin in Admixture. By W. O. Emery..... 665

Commercial Papain and Its Assay. By H. M. Adams..... 669

A Method for the Estimation of Podophyllum Resin. By W. M. Jenkins..... 671

### LABORATORY AND PLANT:

Studies on Filtration. By J. W. Bain and A. E. Wigle..... 672

Scrubber for Chemical Laboratory Vacuum System. By Charles Baskerville..... 675

New Apparatus for Determination of Hydrogen Sulfide in Water—Part I. By Geo. B. Frankforter..... 676

### ADDRESSES:

The Present Patent Situation. By Maximilian Toch.. 677

Some Economic Aspects of Industrial Chemistry. By Bernhard C. Hesse..... 678

Chemical Studies of the Pollution of the Ohio River. By Earle B. Phelps..... 682

The Application of Physical Chemistry to Industrial Processes. By Walter F. Rittman..... 684

Standards of Food and Drug Chemists. By Edward Gudeman..... 687

The Chemist, a Growing Factor in Merchandizing. By A. V. H. Mory..... 689

### CURRENT INDUSTRIAL NEWS:

Chemical Industry and Trade in America in 1913..... 690

Canada's Foreign Trade in Chemical and Related Products..... 691

Recent Increase in Production of Lime Nitrogen..... 692

Further Hydro-Electric Power Undertakings in Norway..... 692

Hydrogenated Fats as Foodstuffs..... 693

Ammonium Sulfate and Sodium Nitrate in 1913..... 693

American Coke..... 693

Labor Conditions in Germany..... 693

A Substitute for Galvanized Iron..... 694

Open-Hearth and Bessemer Rails in America..... 694

Combustion on Gold and Silver Surfaces..... 694

### NOTES AND CORRESPONDENCE:

Relation of Composition of Ash in Coal to Its Fusing Temperature..... 694

The Effects of the Ensilage Process on the Solubility and Metabolism of Floats..... 695

On Analysis of Copper, Tin and Silicon Alloys..... 695

On the Rapid Determination of Copper in Open Hearth and Alloy Steel or in Cast Iron..... 696

Tin Plate and Steel Mill Operations in July..... 696

Platinum in Westphalia..... 696

Cheaper Pig Iron..... 697

PERSONAL NOTES..... 697

GOVERNMENT PUBLICATIONS..... 698

BOOK REVIEWS: Welding and Cutting of Metals; Oxyacetylene Process; The Synthetic Use of Metals in Organic Chemistry; Modern Steel Analysis; Underground Waters for Commercial Purposes; Sugars and Their Simple Derivatives..... 701

NEW PUBLICATIONS..... 702

RECENT INVENTIONS..... 703

MARKET REPORT..... 704

## EDITORIALS

### THE FUTURE OF SCIENTIFIC RESEARCH

For the last fifty years it has been assumed that the proper home for scientific research is the university, and that scientific discovery is one of the most important—if not the most important—function which a university can fulfill. In spite of this only a few of the American universities, which are admittedly among the best equipped and most energetic of the world, devote a very large portion of their energies to research work, while quite a number prefer to divert as little energy as possible from the business of teaching, which they regard as the primary function of the university.

This neglect of research work by the universities is generally deplored by leading scientific men, and one of the objects of the Committee of One Hundred on Scientific Research, appointed by the American Association for the Advancement of Science, is to assist the universities in increasing their facilities for research work and the inducements which they offer to young men to enter into it. But it seems that the time has come for us to consider the whole question of the relation of scientific research to the university; how far that relation will continue, and to what degree we may expect it to be modified in the near future. Looking back on the history of science we can perceive that so far as research work has been associated with institutions, it has always been because those institutions required the results of the research for the effective performance of their own essential duties; and that when the progress of science ceased to be an advantage to the other work of the institution, the furthering of that progress was abandoned.

The earliest scientific men were ecclesiastics, who regarded the knowledge which they derived from their inquiries as a means of developing the fullness of the religious belief both of themselves and of those whom they taught, and who felt that the opening up of the marvels of natural science was a fitting part of worship. As the advance of knowledge came to demand more and more modification of creeds and dogmas, so that the increase of knowledge, instead of being an advantage to any particular religious body, was a danger in that it might introduce dissent and doubt, the ecclesiastical world abandoned the pursuit of natural science, and the mantle which the church dropped fell upon the university.

The readiness of the university to accept the burden of being responsible for the advancement of knowledge was due essentially to the fact that the results obtained were immediately applicable to the purpose of teaching, and that, indeed, only by assiduous investigation and discovery could the facts of natural science be sufficiently correlated to make it possible to present them in orderly manner, so that they could be understood by the immature minds with which a university has to deal. This necessity for continual investigation on the part of a teacher was so marked, and the suc-

cess of teachers who themselves were engaged in fresh investigation was so pronounced, that it was generally recognized that the best advanced training in science could be obtained only under a man who was himself actively engaged in promoting the science which he taught. But of recent years the advancing specialization of science and the complexity of each branch have made it more and more difficult for any but the specialists in that subject to appreciate or even to understand the work which is being done in its advancement until the new results obtained through the pushing forward of the ever advancing frontier of knowledge have been digested and brought into line with the general scheme of the subject; and as it becomes more difficult for the ordinary learner of a science to appreciate the work of those who are advancing the science, so the value of contact with those workers diminishes until now it is even thought by some that the ordinary scientific student is best taught by those who are specialists in teaching rather than specialists in research, and many of the university authorities are beginning to feel, even when they do not actively display, distrust of the research specialist in his capacity as a teacher.

It may be suggested then that there is a possibility that as the progress of scientific research lessened its usefulness to the ecclesiastical profession, so in a similar sense its further progress is beginning to lessen its usefulness to the teaching profession, and if this is so, then we may be sure that, however desirable for the community at large it may be for the progress to go on, yet the universities, whose primary and essential business is teaching, will feel less and less at liberty to divert energy from teaching to work which has no direct bearing upon their own chief function.

This view will, of course, be unwelcome to those who hold—as does the writer—that the progress of scientific research is the progress of the human race, and that the race or people or nation which devotes the most time and energy to the furtherance of research will itself be the leader in civilization. But, however important one may feel the progress of research to be, nothing can be gained by merely insisting that it shall be continued by institutions to whom its benefit is diminished, and our energies should, therefore, be directed towards the development of institutions which will prosecute scientific research because it in turn is of use to them as in the past it has been of use to the ecclesiastical and to the teaching professions.

In the case of the natural sciences the usefulness of investigation to the teacher still continues, so that in agriculture and biology and in such subjects as philosophy or psychology the universities are very active in advancing the frontiers of knowledge, but in the physical sciences this is much less the case, and it is for these sciences that some new form of institution, which is actively interested in the results, is required to supplement the activities of the universities.



Fortunately, it seems as if such an institution is already available and that we may hope before long to find new hands prepared to take up the responsibility for the execution of scientific research, as the universities may find it necessary to be relieved of it.

For many years the greatest gainers by the direct progress of scientific knowledge have been the manufacturing industries, and ever since their start they have been coquetting with the idea of advancing scientific progress directly, and of turning it into those directions which seem to be of immediate advantage to themselves.

When research laboratories were first started by industrial corporations the men employed in them were expected to confine their attention very strictly to the immediate requirements of the industry with which they were associated, and general investigation even of the general theory of the industry itself was discouraged, while publication of original work done in such a laboratory was regarded as almost out of the question. Wider experience, however, has shown that the more general the work done by the research laboratory, the greater are the results reaped by the industry likely to be, while the advantage to the worker of being allowed to publish any results of general, as opposed to technical, interest, has become so obvious that all the more important laboratories permit free publication of scientific papers. It seems likely that the proportion of purely scientific work done in the research laboratories will increase rapidly as the advantages of such fundamental theoretical work to industry become better known, and it would not seem too much to hope that before long the industries will devote themselves to scientific research with a definite enthusiasm and energy which must make them the predominant factors in the production of new knowledge. So that it would appear that it is to the industrial research laboratories that we must look in the future for progress in all branches of science which are affiliated in any way with manufacturing industries.

Organic chemistry has for some years been advanced largely through the work of men associated with industrial corporations; analytical chemistry shows every sign of following in the same path, while the other branches of chemical research are so closely associated with industry that they will be adequately provided for in the immediate future. In physics, electricity

and optics are already directly associated with large and important industries maintaining adequate research laboratories, and the other branches of physics will surely be associated in due course with cognate industries.

It must be stated, however, that there are some branches of science—and these by no means the least important ones—which have so little direct relation to industry that the industrial laboratories will certainly neglect them to some extent, and it is for these branches of science, which may be termed the “non-paying” ones, that special provision must be made.

The whole argument of this article is intended to show that only an institution which benefits by the knowledge which is developed can be expected adequately to provide for the furtherance of that knowledge, and if the industries do not directly profit by the advancement of some branches of science, and yet the progress of those branches is essential to the welfare of the people as a whole, it is the people as a whole that may be justly expected to provide for their advancement. This is already recognized in the case of some branches of science which have a more obvious and direct bearing on the general life of the community. Agriculture, forestry—even zoology in some of its phases, such as entomology and pisciculture—are already provided for by state or federal institutions, but new institutions are urgently required for theoretical physics, theoretical chemistry, mathematics and some other branches of physical science. Astronomy is provided for by private benefaction, provision for the means of obtaining knowledge about the universe at large having apparently been regarded by a number of wealthy men as a deserving object of charity. It would seem, therefore, that the energies of those who are interested in the furtherance of scientific research should be directed toward obtaining adequately staffed and equipped institutions for the prosecution of those sciences which have little direct relation to industry, leaving the furtherance of the branches of science directly associated with manufacturing processes to the industrial laboratories, which are now rapidly springing up to take their share in the advancement of knowledge.

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## ORIGINAL PAPERS

### OZONE IN VENTILATION<sup>1</sup>

By J. C. OLSEN and WM. H. ULRICH

In spite of the fact that a great many investigations have been carried out in recent years on the effect of ozone on air bacteria and odors and also on the physiological effects of ozone, the most diverse conclusions have been reached and opinions expressed with reference to the questions investigated. This confusion is due somewhat to faulty scientific technique and

deductions from improperly chosen experiments as well as *ex parte* point of view. The most recent criticisms against ozone in ventilation are found in two articles which were published in the issue of September 27, 1913, of the *Journal of the American Medical Association*, one by Jordan and Carlson and the other by Sawyer, Beckwith and Skolfield on the bactericidal, physiologic and deodorizing action of ozone. A number of errors in the methods used in the experiments given in these articles have been noted and these seem so serious and the articles have been so

<sup>1</sup> Read at the 6th Semi-annual Meeting of the American Institute of Chemical Engineers, Troy, New York, June 17-20, 1914.

widely quoted that it seems desirable to correct the misapprehensions which have been produced. Both of these articles refer to the fact that exaggerated claims were made by agents selling ozone machines.

In the article by Jordan and Carlson, it is stated, on page 16, that the concentration of ozone is determined by drawing the ozonized air through a solution of potassium iodide which has been acidified with sulfuric acid. The liberated iodine is then titrated with thio-sulfate solution. It is well known among chemists that an acidified solution of potassium iodide is readily oxidized by the ordinary oxygen of the air, and, therefore, if an acidified solution of potassium iodide is used for the determination of ozone, the results will be high. The amount of the error will vary with the concentration of the ozone and may easily give results double the true concentration of ozone. This error can easily be demonstrated by drawing air free from ozone through such an acidified solution of potassium iodide. It is evident, therefore, that no reliance can be placed on the figures given for the concentrations of ozone which are reported in this article. In the article by Sawyer, Beckwith and Skolfield, the concentrations of ozone were not determined.

It is universally recognized by ventilating engineers who are familiar with the use of ozone that it is of the greatest importance to regulate the concentration of the ozone and that ozone is useful only when employed in the proper concentration. This well known principle seems to have been so little understood by these investigators that they failed to make careful and accurate determinations of the concentrations of ozone used and therefore many of the conclusions which they reached are entirely vitiated.

Another very serious error in experimental procedure is found in the tests which were made on the effect of ozone on odorous substances. A considerable number of such substances were experimented with and the conclusion was reached that the ozone *masks* these odors but does not destroy them and that, therefore, ozone is not useful in the removal of such odors.

The method of procedure consisted in exposing the substance giving off the odor until a marked odor was noticed in the small closed room which was used for the experiments. The ozone machine was then operated until a strong odor of ozone was produced. Observations were made from time to time of the odor in the room and it was observed in a good many cases that the ozone odor gradually disappeared and the odor of the substance experimented upon returned. In some cases ozone was again generated until its odor was pronounced and observations again made with reference to the disappearance of the ozone odor and the reappearance of the odor of the substance experimented upon. The conclusion was drawn that the ozone did not destroy the substance giving the odor but masked it; this conclusion was based upon the disappearance of the ozone odor and the return of the other odor. No other evidence, whatever, on this point is presented.

In these experiments, no attempt seems to have been made to determine the amounts of the odorous

substances which were present in the air except by the odor. The experimenters apparently did not consider the fact that the odors of substances differ a great deal in intensity and that the quantities of substances which would be present, even though the intensity of the odor was the same, would differ very much. These authors also failed to keep in mind that the destruction of odors by ozone is an oxidizing process and that this, as well as all chemical reactions, is quantitative in the sense that a definite amount of oxygen is required to oxidize a definite amount of an oxidizable substance.

The following reaction takes place when ozone oxidizes hydrogen sulfide:



That is, 34 parts of hydrogen sulfide would require 48 parts of ozone for their oxidation. When the hydrogen sulfide is dissolved in water, the sulfur liberated is still further oxidized by the ozone to sulfuric acid which would require a still larger quantity of ozone, but according to the reaction given, a somewhat larger amount of ozone than hydrogen sulfide would be necessary for the destruction of this substance. Now, if the intensity of the ozone odor is much greater than that of the odor of hydrogen sulfide, the hydrogen sulfide would be oxidized by the ozone in the experiments reported by Jordan and Carlson and some other authors quoted, and the hydrogen sulfide odor would then return as reported by these investigators.

In order to verify these conclusions, experiments were carried out to ascertain the amount of hydrogen sulfide which will give a distinct odor. A large balloon flask of 30 liters capacity was used. The hydrogen sulfide was produced by treating known weights of carefully analyzed iron sulfide with dilute sulfuric acid. The reacting substances were placed on a watch crystal suspended in the center of the balloon flask. In addition to the odor, tests were made with lead acetate paper.

INTENSITY OF ODOR OF HYDROGEN SULFIDE		
Mg. H <sub>2</sub> S PER CUBIC METER	TEST WITH LEAD ACETATE PAPER	ODOR
977	Very black	Very strong
244	Very black	Strong
61	Very black	Distinct
30	Turned black slowly	Fairly distinct
15	Brown on edges	Faint
7.6	Turned brown very slowly	No odor

While to obtain a distinct odor of hydrogen sulfide, 61 parts are required, the odor of ozone is very marked when present to the extent of one part per million, the limit being one-tenth part per million. In the experiments of Jordan and Carlson, the concentration of the hydrogen sulfide must have been from 30 to 60 mg. One part of ozone would have given a strong odor which could mask the odor of the hydrogen sulfide until, by the oxidation of the latter, the ozone was decomposed. Less than one part per million of the hydrogen sulfide would be destroyed by this oxidation, leaving a sufficient amount of hydrogen sulfide to give a very distinct odor. On again generating ozone until a strong ozone odor was obtained, the hydrogen sulfide would be again "masked," and when the ozone odor had disappeared the hydrogen sulfide odor would reappear. This could be done repeatedly

as reported by Jordan and Carlson. The conclusion which they drew, however, is entirely unjustified, namely, that their experiments showed that the hydrogen sulfide odor was merely masked and hydrogen sulfide not oxidized or destroyed by the ozone.

In order to verify this conclusion, the following experiment was carried out: A concentration of 25 mg. of hydrogen sulfide was treated with ozone of a concentration of 35.6 mg. per liter. In these concentrations there would be just enough ozone to oxidize the hydrogen sulfide. In this experiment the ozone odor was at first very pronounced but after this odor had disappeared there was no hydrogen sulfide odor. A slight acidity was indicated by the reddening of blue litmus paper. The ozone used had been very carefully tested for nitrous oxides but none were found.

Another experiment was carried out in which the ozone concentration was 7.6 parts per million, while the hydrogen sulfide concentration was 60.7 mg. per cubic meter so that only a small part of the hydrogen sulfide could be oxidized by the ozone present. At first only the odor of the ozone could be detected. The hydrogen sulfide odor gradually returned so that within one hour a faint and after two hours a distinct hydrogen sulfide odor was detected while the ozone odor had entirely disappeared.

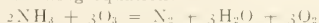
This experiment could be repeated three or four times, as reported by Jordan and Carlson on page 33 of their article. They further state: "The mechanism of this masking action of ozone does not concern us here." If the authors had considered the "mechanism" of this action, they might have reached entirely different conclusions and would have seen that their experiments were in exact accordance with the theory that ozone oxidizes hydrogen sulfide and other substances. They still further refer to the fatigue of the olfactory end-organs by the ozone. They say "Strong concentrations of ozone rapidly fatigue or anesthetize the olfactory epithelium." One wonders why the authors did not make this statement general and state what every chemist has frequently observed that *hydrogen sulfide* and the numerous other odors which are present in chemical laboratories produce the same effect on olfactory epithelium so that these odors are not noticed by workers in the laboratory.

Hydrogen sulfide is also oxidized by the air as is shown by the fact that the odor slowly disappeared in a duplicate experiment in the absence of ozone.

In some cases ozone acts as a catalytic agent. This was shown by the action of ozone on linseed oil. Weighed quantities of linseed oil were exposed to air and ozone. The oil exposed to air gained 17 mg. while an equal quantity exposed to the action of ozone gained 110 mg. during the same time. The amount of ozone generated was 11.4 mg. The ozone, therefore, acted as a catalytic agent, causing the absorption of 82 mg. of oxygen which is nearly five times as much oxygen as was absorbed by the oil exposed to air alone. It is reasonable to suppose that ozone would act as a catalytic agent and cause the oxidation of other oils and organic substances similar to linseed oil.

In the case of ammonia, the same considerations

apply. Ammonia is oxidized by ozone in accordance with the following equation:



In this case, one part of ammonia is oxidized by about four parts of ozone. A study of the intensity of the odor of ammonia gave the following results:

INTENSITY OF THE ODOR OF AMMONIA		
MG. NH <sub>3</sub> PER CUBIC METER	TEST WITH LITMUS PAPER	ODOR
1000	Turns blue readily	Strong
659	Turns blue slowly	Fairly strong
329	Turns blue slowly	Fairly strong
165	Turns blue very slowly	Fairly strong
82	Turns blue very slowly	Quite distinct
41	Turns blue on edges very slowly	Faint
21	Turns partially blue on edges very slowly	Very faint
10	No action	No odor

Experiments were carried out in which known amounts of ammonia were treated with definite amounts of ozone and the ammonia remaining was determined by absorption with sulfuric acid and nesslerizing. Ammonia is acted upon very slowly so that 24 hours were allowed for the reaction. The concentration of the ozone was 35.6 mg. and of the ammonia, 125 mg. per cubic meter. After 24 hours, 78 mg. of ammonia remained in the flask containing air and 75 mg. in the flask containing ozone. The quantity of ozone present was sufficient to oxidize 8½ mg. of ammonia per cubic meter. The experiment indicates some oxidation of ammonia by ozone. Erlandsen and Schwartz<sup>1</sup> state that their results showed no action of ozone on ammonia.

Experiments were also carried out to ascertain the intensity of the odor of oil of cloves. It was found that 66 mg. per cubic meter would give a strong odor. The amount of ozone necessary to oxidize oil of cloves cannot be calculated exactly but it would probably require several times more than an equal weight. On subjecting the oil of cloves vapor in a concentration of 36.6 mg. per cubic meter to the action of ozone of a concentration of 33 mg. per cubic meter, it was found that at first a distinct odor of ozone could be detected which gradually disappeared and was replaced by a sweet odor which had no resemblance to the strong odor of the oil of cloves. Very evidently the oil of cloves or one of its strong smelling constituents is oxidized, at least partially, so as to leave an organic compound having an entirely different odor. The flask was allowed to stand a total of 21 hours although the reaction was practically complete within 2 to 3 hours. The reaction did not seem to be entirely regular. The experiment was repeated several times and the formation of the sweet aromatic substance repeatedly observed but at times the odor of cloves persisted. Any excess of ozone was removed by shaking with 10 per cent ferrous sulfate solution. Control experiments were also made with a balloon flask containing oil of cloves and air only. Erlandsen and Schwartz have made a similar observation with respect to skatol and indol. They state that these substances are completely decomposed by ozone with the formation of pleasant smelling substances similar to coumarin. They also state that mercaptan is rapidly decomposed by a large excess of ozone. These authors also found that hydrogen sulfide is oxidized by ozone. Jordan

<sup>1</sup> *Zeit. of Hyg.*, 1913, pp. 81-100.



and Carlson also mention the work of Erlandsen and Schwartz but state that the results of the latter agree with those of Jordan and Carlson in showing that ozone masks odors and does not oxidize the substances discussed. Jordan and Carlson even state that "The inability of ozone to oxidize (to any appreciable extent) ammonia vapor and oil of cloves is very striking." Franklin gives the results of experiments showing the oxidation of a great many organic substances and demonstrated that carbon monoxide is oxidized to carbon dioxide.<sup>1</sup>

Undoubtedly many of the conflicting conclusions which have been reached are due to the failure of experimenters to take into account the quantitative relations between ozone and the substances to be oxidized and have generally failed to realize that on account of the much greater intensity of the odor of ozone than that of other substances producing odor far too little ozone has been employed in the experiments. The odor of ozone is at least 100 times as intense as that of other substances having a pronounced odor.

The common method of using ozone to destroy odors seems to be justified by these considerations. The ozone machines in good practice are operated so that a very small concentration of ozone in the air is produced. The continued renewal of this small amount of ozone oxidizes the odorous substances and gives the total quantity of ozone required by chemical theory.

Jordan and Carlson undertook to prove that ozone does not destroy smoke by coating a piece of glazed paper uniformly with a thin film of lampblack and subjecting the carbon to the action of ozone for 10 hours and state that there was no effect on the lampblack. They regard this as evidence that ozone does not destroy smoke although they state that smoke also contains carbon monoxide, sulfurous acid, etc. They seem to have made no attempt to study the effect of ozone on carbon monoxide and sulfurous acid but state that the assertion that "ozone destroys smoke" is equivalent to a deliberate deception because ozone does not oxidize carbon particles suspended in the air. Not being chemists, Jordan and Carlson might not have known that carbon is extremely difficult to oxidize but they should have known that carbon monoxide and sulfurous acid as well as creosote and other pungent and aromatic organic substances present in smoke produce disagreeable and toxic physiological effects. It is just these constituents of smoke which are easily oxidized by ozone. The carbon which is not acted upon is totally inert and harmless.

Jordan and Carlson also carried out investigations on the action of ozone on air bacteria. As has already been stated, their determinations of the concentration of ozone cannot be relied upon because acidified solutions of potassium iodide were used which give high results. The authors admit that the plate method which they used was not an exact one and that therefore the results were irregular. They obtained a reduction of bacteria from 64 to 38, 49 to 18, 61 to 67 (increase), 78 to 34; that is, the bacteria were reduced to 40.6 per cent, 63.3 per cent and 56.4 per cent in

three tests, while in the fourth there was an increase to 109.8 per cent. Most authors would discard the fourth test and consider the reduction to be about 55 per cent. Jordan and Carlson then tried Winslow's more exact method but did not use a large enough sample for the test (4.5 liters) so that the highest number of bacteria counted was 7. It is not good practice in bacteriological work to rely on counts of so small a number. Jordan and Carlson draw the following strange conclusion from their results:

"2—The alleged effect of ozone on the ordinary air bacteria, if it occurs at all, is slight and irregular even when amounts of ozone far beyond the limit of human physiological tolerance are employed."

There is no reason to suppose that the ozone used in these experiments was "Far beyond the limit of human physiological tolerance." The reduction in the number of air bacteria is not "slight and irregular." The experimental results of Jordan and Carlson agree with the results obtained by one of us<sup>1</sup> in New York school rooms showing a reduction in air bacteria and moulds of 75 per cent, 91 per cent and 91 per cent, the greater reduction resulting from longer exposure to ozone. No ill effects were observed on the children and adults present during these tests.

Jordan and Carlson (p. 34) state: "Some bacteria are undoubtedly killed by ozone, especially if they are in a moist condition." This statement is correct as it is generally recognized that ozone destroys moist bacteria very rapidly. The conclusion drawn by Jordan and Carlson is very far from being correct. They say: "In practice, however, the fact is of very slight importance." The works of Chapin, Doty and of Winslow and Robinson have fairly disproven the belief held so long that bacteria existed as a menace in rebreathed air. It has been shown that infection occurs but rarely from air-born bacteria and then only when the bacteria are in the moist condition. It is just these virulent bacteria which are quickly destroyed by ozone even in low concentrations. The bacteria which resist the ozone are powerless to transmit disease.

It is by no means necessary to show that ozone is capable of sterilizing the air in order to show that it is useful in ventilation. There is in fact no other disinfectant which can be used even in low concentrations in living rooms. All other known disinfectants are highly dangerous in concentrations high enough to be at all effective. Ozone in low concentrations will both remove odors and will materially reduce the bacteria content of the air.

Jordan and Carlson attempted to show that ozone is dangerous by subjecting guinea pigs to high concentrations until the animals died. They also forced strong ozone (10 parts per million) directly into the lungs of dogs and rabbits after performing tracheotomy under ether and inserting a tube well below the larynx and treating the wound with cocaine. They say they did this because at least three-fourths of the ozone is decomposed by the mucous membrane of the respiratory

<sup>1</sup> "Purification of Air and Water by Means of Ozone," Olsen, Fourth International Congress of School Hygiene.

passages. It is difficult to see what bearing this experiment can have on the use of ozone in ventilation. The ozone which was forced into the lungs must have been several hundred times as concentrated as it is ever used in ventilation. It would have been quite as logical to place animals in pure oxygen or even in an atmosphere of 50 per cent oxygen and also force these gases directly into the lungs. When the animals died and the lungs were found to be inflamed, the conclusion might be drawn by highly academic experimenters that it is dangerous to breathe air containing 20 per cent oxygen.

Jordan and Carlson carried out experiments with what might be called low concentrations of ozone. They subjected 4 cats, 4 rabbits, 6 guinea pigs and 12 rats to ozone of 1 part per million nine hours daily during two weeks so that irritation of the eyes and nose was produced. Body weight, appetite and general condition were noted. No ill effects on appetite and body weight or general condition could be observed. The conclusion could, therefore, be drawn that ozone in moderate concentrations is harmless but Jordan and Carlson warn us that this conclusion is not justified.

They say: "We desire to state, however, that this test does not warrant the conclusion that the ozone in concentrations that may be used in practical ventilation is harmless to man. Two weeks is a short time in the life of a man. If ozone in ventilation should come into general use, it would mean in the case of office and shop workers exposure to ozone from six to ten hours a day, six days of the week, from nine to twelve months of the year for from twenty to fifty years. And even if this prolonged exposure to ozone should prove harmless to the robust person, what about the unfortunate person whose lungs have only slight power of resistance?"

Jordan and Carlson seem to have fallen into the error of assuming that because they have not tried to, and therefore have not demonstrated actually, benefit from the use of ozone, this is equivalent to having demonstrated the reverse, *i. e.*, the harmfulness of ozone.

If the facts presented in this paper are properly interpreted they will be found to be in accordance with the view that ozone is a powerful disinfectant and deodorizing substance, which, in suitable concentration, is without any injurious effects whatever. The elimination of odor is by no means the least important function of ozone and there is no other agency available except dilution with fresh air. In many cases it is impossible to introduce enough air for this purpose without producing annoying and dangerous drafts of air not to mention expense of blower installation and operation as well as heating the air. As a matter of fact, before ozone was available, disagreeable odors have often been considered unavoidable nuisances which could not be eliminated or overcome.

With reference to the alleged harmful effects of ozone, no single instance of harm to a person from the proper use of ozone in ventilation has been published but all adverse opinions have been deduced, by inference, as in the paper by Jordan and Carlson, from

experiments performed with very high concentrations while all efforts to produce harm experimentally with weak ozone have failed.

Jordan and Carlson report that twenty-six animals, exposed for fourteen days, during nine hours each day, to concentrations high enough to cause irritation of the eyes and nose, suffered no ill effect whatever. Hill cites the cases of the numerous workers in the London underground tubes who have shown no ill effect in three years. Gminder cites the unharmed workers in the spinning mills at Reutlingen, and numerous similar instances of prolonged proper use of ozone without a single complaint are today in existence. The Jordan and Carlson report is the most elaborate and convincing laboratory test that has been published.

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### THE FLUORESCENCE OF PETROLEUM DISTILLATES<sup>1</sup>

By BENJAMIN T. BROOKS AND RAYMOND F. BACON

Fluorescence is one of the most striking characteristics of petroleum distillates but its cause is not known, at least some of our best authorities attribute it to causes which have nothing to do with the phenomenon. The heavier distillates from Pennsylvania and certain other crude petroleum have a marked greenish fluorescence, and the trade has come to associate this property with Pennsylvania oils. For some uses it is common practice to "debloom" the oils by sun-bleaching or by the addition of certain "deblooming" substances. The subject therefore has some practical as well as theoretical interest.<sup>2</sup>

Engler considers that the fluorescence of mineral oils is due to their colloidal character. Crude oils and the heavier distillates are optically nonhomogeneous and show a marked Tyndall effect, but this property cannot be considered as indicating colloidal properties since many organic compounds having large molecular weights show the Tyndall effect when in true solution. Schneider and Just<sup>3</sup> claim to have observed ultramicroscopic particles in a "yellow mineral oil" and a sample of "paraffin oil." Holde,<sup>4</sup> studying the physical condition of lime soaps in grease, stated that colloidal particles are not discernible as such under the microscope. It is probable, however, from the researches of Holde that such greases, as well as oils containing asphaltic or resinous matter, are to be regarded as colloidal, not true solutions. Schulz<sup>5</sup> claimed that the effect of adding "deblooming" substances, such as nitrobenzol and nitronaphthol, was merely that of adding something having a high refractive index, thus making the oil optically homogeneous.

This theory of the fluorescence of mineral oils seemed very plausible. However, since many examples of nonfluorescent oleo-resinous solutions and mixtures

<sup>1</sup> Presented at the 49th Meeting of the American Chemical Society, Cincinnati, April 6-10, 1914.

<sup>2</sup> Cf. "Relations between Physical Properties and Constitution," Kayser, "Handbuch d. Spectroscopie," Vol. IV, p. 839; Kauffmann, "Beziehungen zw. Fluoreszenz u. Chem. Constitution," *Samm. Chem.-u. Chem. techn. Vorträge*, 11, 1906.

<sup>3</sup> *Z. f. wissenschaftl. Mikroskopie*, 1905, p. 489.

<sup>4</sup> *Z. f. angew. Chem.*, 31 (1908), 2138; *Koll. Ztschr.*, 8 (1908), 270.

<sup>5</sup> *Petrol. Berl.*, 8, 205.

are known and since the fluorescence of mineral oils persists after repeated distillation and is quite marked in distillates boiling as low as  $200^{\circ}\text{C}.$ , we believed that resinous or asphaltic matter could not be a contributing factor. Our experiments have shown that, in general, oxidizing agents partially or wholly destroyed the fluorescence. Certain facts suggested to us that sulfur or carbon in colloidal suspension might be the cause of the phenomenon. Stable colloidal suspensions of carbon, in water and various organic liquids, have been prepared<sup>1</sup> and described as nonfluorescent and brown to black in color. Sulfur, on the other hand, often shows bluish colors when in colloidal degree of dispersion and the blue color of ultramarine blue is undoubtedly caused by so-called colloidal sulfur.<sup>2</sup>

We have succeeded in proving that colloidal suspensions have nothing to do with the fluorescence of mineral oils.

Working on the theory that ultramicroscopic particles were present, 100 cc. of a highly fluorescent lubricating oil were diluted with kerosene to about 500 cc. in order to decrease the viscosity. The solution was placed in a suitable cell containing two round copper plates spaced 2 cm. apart. The oil between the plates was subjected to a unit direction field of 30,000 volts potential difference for thirty minutes without any visible change in the fluorescence or flocking out of any kind of substance.

A sample of the same solution, carefully dried by calcium chloride, was filtered through the finest filter paper and examined under an ultramicroscope of the Zsigmondy-Siedentopf type but no particles whatever were visible. It was found that unless the oil was carefully dried and filtered, particles were visible in the light cone. These may have been minute drops of water or dust. The fact that the ultraviolet light cone is made visible to the eye with bright fluorescence has no significance so far as the colloid theory is concerned since as a general rule the wave length of the emitted fluorescent light is always greater than the incident ray, in this case from ultraviolet to visible blue. Furthermore, the ultraviolet cone contains a certain amount of the visible rays. No more rigid proof of the non-existence of substances in colloidal suspension in carefully purified fluorescent mineral oil, could be desired. In order, further, to test the arrangement and efficiency of our instrument, a colloidal gold "solution" was made by the formaldehyde reduction method, one of platinum by the Bredig method, and one of palladium by reducing with hydrogen according to Paal, and the beautiful results characteristic of this instrument were obtained.

Percolation through Fuller's earth is an excellent and well known method for clarifying and bleaching oils. A sample of a highly fluorescent lubricating oil was allowed to run through a five foot tube packed with fine Fuller's earth. The resulting oil was very light in color but highly fluorescent and when a little tarry matter, which gave brown nonfluorescent solutions in

kerosene, was added to the oil until the color matched the original oil, the two could not be distinguished. The fluorescent material is therefore only slightly absorbed by Fuller's earth and is probably not of very great molecular complexity.

While working on the colloidal suspension theory, the marked solubility of sulfur in mineral oils was noted. A 200 cc. sample of a light machine oil was heated to  $100^{\circ}\text{C}.$  with an excess of flowers of sulfur, filtered hot, and on cooling about 0.5 gram of sulfur crystallized out. Guiselin<sup>1</sup> states that benzine dissolves 0.5 per cent sulfur at  $20^{\circ}\text{C}.$  It is extremely improbable that a stable colloidal suspension could exist in which the solubility of one phase in the other is as great as in the case of sulfur and petroleum oils.

Carbon disulfide added to a fluorescent lubricating oil weakens the fluorescence almost to the point of extinction; what remains is dark greenish. Before making the experiments with the ultramicroscope, this was thought to favor the sulfur suspension theory, or the theory of Schulz based on optical homogeneity.<sup>3</sup>

Further experiments with other solvents showed that the character of the fluorescence was affected by the various common solvents in the same way as in the case of the diamino derivatives of terephthalic acid methyl esters, studied by Kauffmann.<sup>3</sup> The effect of the various solvents was even more marked with solutions of the purified fluorescent material described below. The fluorescence colors observed were as follows:

Amyl alcohol.....	Brilliant sky-blue
Aniline.....	Very faint green, no blue
Benzol.....	Pure clear blue
Carbon bisulfide.....	Faint green, no blue
Chloroform.....	Bluish green, passing into green on concentrating
Ether.....	Clear blue
Ligroin.....	Blue
Phenol.....	Greenish blue
Pyridine.....	Bluish green

In most cases the addition of small amounts of solvents having high refractive indices has practically no effect on the fluorescence. The effect of adding nitro compounds therefore must have an explanation different from that offered by Schulz.

The introduction of a nitro group into the molecule of a fluorescent benzol derivative, such as the terephthalic esters, completely destroys its fluorescence. It appears that a nitro group in the solvent has the same effect as a nitro group in the molecule of the active compound itself. This is not surprising in view of the marked effect of other solvents. We believed that possibly the fluorescent substance in mineral oil owed this property chiefly to the presence of one or more amino groups as auxochromes but, as will be shown below, this cannot be the case. Although we have found that oxidizing agents destroy the fluorescence, it is probable that the action of nitro compounds is purely physical since we have added  $\text{N}_2\text{O}_4$ , nitrated kerosene or nitrobenzol to fluorescent lubricating oils chilled to  $-10^{\circ}\text{C}.$  and destroyed the fluorescence. It is highly improbable that oxidation of any hydrocarbons could take place under these conditions since

<sup>1</sup> Thomae, *Koll. Ztschr.*, **11** (1912), 268; Vanzetti, *Koll. Ztschr.*, **13** (1913), 6.

<sup>2</sup> Laesegang, *Koll. Ztschr.*, **7** (1910), 307; Hoffmann, *chem. Ztg.*, **1910**, p. 1079.

<sup>3</sup> *Petroleum*, **1913**, p. 1309.

<sup>2</sup> The refractive index of carbon bisulfide is  $n_D^{20} = 1.6276$ . *Ann. d. Chem.* (Liebig), **393** (1912), 1.



at 0° C., N<sub>2</sub>O<sub>4</sub> merely adds on to ethylene bonds without oxidation.<sup>1</sup> There is also the possibility that such compounds as picric acid and nitrobenzol form non-fluorescent addition products, or double compounds, such as is the case with pyrene and chrysene. However, the simple nitro paraffines are not known to form such double compounds and "nitro kerosene" is fully as efficacious as nitrobenzol for neutralizing fluorescence. The following experiment is interesting in this connection: A sample of a highly fluorescent lubricating oil was "debloomed" by the addition of nitrobenzol. This oil was then shaken out six times with one-half its volume of 96 per cent alcohol, after which treatment the blue fluorescence had reappeared and exactly matched a sample of the same oil not treated with nitrobenzol, but shaken out with alcohol in the same way as the first sample. Refining such a "debloomed" oil with sulfuric acid yields a fluorescent oil identical in this respect with that obtained by refining the original oil. The action of nitro compounds in neutralizing fluorescence must therefore be purely physical in character.

The fact that exposure to the atmosphere for some time partially destroys and changes the character of the fluorescence suggested that what took place during this process was slow autoxidation.

Nitrous acid readily neutralized the fluorescence of lubricating oils, but the oils gradually became dark colored and resinous. Distillation of the latter dark colored oil *in vacuo* or with superheated steam yielded oil having a bluish fluorescence. Repeated washing with alkali removes only a small part of the coloring matter. Shaking a part of a sample of pale engine oil with nitrous acid for three minutes, followed by washing with water and filtering through Fuller's earth, gave a less resinous, light colored oil, very similar to that obtained by sun-bleaching. Oxides of nitrogen, generated by the action of dilute nitric acid on a metal, were then tried and it was found that the sun-bleached oil could be matched, with respect to color and fluorescence, provided the temperature of the oil was not permitted to rise above 10° C., before washing with dilute alkali. At low temperatures addition of oxides of nitrogen to unsaturated compounds probably results as shown by Jegorow. Unless the oil is chilled before passing in the oxides of nitrogen, oxidation appears to result, accompanied by rise in temperature, darkening in color and formation of resinous material. No method of removing the resinous coloring matter without at least partially restoring the bluish fluorescence was found. The effect, on the color of the oil, of nitric acid in sulfuric acid when used for refining is well known and constitutes one of the advantages of acid made by the contact process over that made by the chamber method.

We then made a series of experiments to determine the chemical properties of the fluorescent substance. The efficiency of sulfuric acid, particularly fuming acid, in removing fluorescence is well known. It was found that the wash water from freshly prepared acid sludge tar, made by refining lubricating stock, was highly fluorescent. This suggested that the

fluorescent material formed water-soluble sulfonic acids, or that the fluorescent substance was a base and removed as a soluble sulfate. The latter hypothesis can hardly be true since dilute acids do not extract the fluorescent material from the oil. A quantity of such fluorescent aqueous solution was made alkaline and extracted with ether but no fluorescent material was obtained indicating that the substance in question is not a base. A dilute acid solution of the fluorescent substance was nearly neutralized with lime to remove the excess of sulfuric acid. The filtered aqueous solution was evaporated nearly to dryness and the crystalline residue, containing sulfate of lime, extracted with alcohol. Twelve liters of lubricating distillate yielded, in this way, about 1 gram of an impure crystalline residue which was intensely fluorescent when dissolved in the different solvents named above. The amount obtained was too small to be thoroughly investigated, but we hope that we shall have an opportunity in the near future to prepare a quantity of this highly interesting material sufficient for further work. The above results were enough to show the general character of the substance. The crude fluorescent substance probably contains one or more compounds of the benzene series resembling or perhaps identical with chrysene, fluorene or pyrene. Such compounds are known to be formed by the pyrogenic decomposition of many organic substances. Klauudy and Fink, in 1900, isolated a yellow crystalline substance, giving highly fluorescent solutions from the residuum of a cracking still. They give it the formula C<sub>24</sub>H<sub>18</sub>.

A large proportion of the fluorescent substance or substances is formed during the distillation of the crude. This was shown by distilling a sample of Oklahoma crude at atmospheric pressure and under a pressure of 5 mm. of mercury. The distillates in the first series were very much more fluorescent than the latter. This is also true of the distillates from coal when distilled at atmospheric pressure and under a pressure of 5 mm. Parallel with this difference it should be noted that substances of the benzol series form a much greater proportion of the coal tar obtained at ordinary pressures, paraffines and olefines constituting over 80 per cent of the coal tar obtained by distilling *in vacuo*.<sup>1</sup> It is also well known that no fluorescent substances are known belonging to the paraffin series.

Halogenation destroys the fluorescence, as is to be expected. Hydrogenation also destroys it.

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## THE MANUFACTURE OF ETHYL ALCOHOL FROM WOOD WASTE—PRELIMINARY EXPERIMENTS ON THE HYDROLYSIS OF WHITE SPRUCE<sup>2</sup>

By F. W. KREISSMANN

### THE PRESENT VALUE OF WOOD WASTE

The value for most of the wood waste produced today is limited to its fuel value for the production of power at the mill. In some cases, methods of closer utilization have been worked out, but compared with the

<sup>1</sup> Jones and Wheeler, *J. Chem. Soc. (London)*, **1914**, 140

<sup>2</sup> Presented at the 49th Meeting of the American Chemical Society, Cincinnati, April 6-10, 1914.

<sup>1</sup> Jegorow, *J. prakt. Chem.*, **86** (1912), 512.

total amount of wood waste produced, the amount of material so utilized is almost negligible. Furthermore, most of the large lumber mills produce waste greatly in excess of the amount necessary for power production and the waste burners are still in use, involving not only a loss of large amounts of wood, but also a definite fixed charge to get rid of it. The utilization of this material is limited, due to a number of considerations which may be classified as follows:

1—LARGE BULK—The bulkiness of the waste material makes a minimum amount of handling imperative and almost prohibits its transportation.

2—MECHANICAL CONDITION OR FORM—The mechanical condition or form of the waste is one of the greatest stumbling blocks to its more complete utilization. Sawdust and shavings are too finely divided to be of value for paper and pulp production or for destructive distillation. For the former, the fiber length has not only been reduced, but the fibers have also been torn and lacerated much as in the production of mechanical ground wood. The destructive distillation of sawdust and shavings is not practicable for two reasons: *First*, the small size of the material makes it such a poor conductor of heat that it is impossible to char it completely in the ordinary forms of retorts and kilns in use; *second*, the charcoal produced is so finely divided that it is difficult to cool and handle and there is no ready market for it. In addition, the waste, as it comes from the mill, is usually a mixture of all the forms enumerated above and any attempt at a separation other, perhaps, than a simple blowing or screening to remove the very fine stuff will increase the cost of the raw material to a prohibitive figure, as shown by the experience of several pulp and paper mills in the yellow pine region of the south. A satisfactory process, therefore, for the utilization of wood waste should be able to handle practically any and all forms of waste as they happen to come from the mill.

3 NON-HOMOGENEITY AND NON-UNIFORMITY Except in some cases, as in factories using only one or two species of wood or in some mills manufacturing only a few species, as, for example, the "yellow pine" (longleaf, shortleaf, loblolly) mills of the south, the non-homogeneity of the waste has operated against its efficient utilization, for many processes such as pulp and paper or destructive distillation require particular species to give a yield and quality of product that will make the processes commercially feasible.

#### THE VALUE OF WOOD FOR ALCOHOL PRODUCTION

All woods, however, have one point in common and that is the fact that they all contain more or less cellulose which makes up the fibers of the wood along with an incrusting substance called "lignin." Any process which could chemically utilize this cellulose would, therefore, overcome the objections laid down above as the form of the material, length of the fiber, species, etc., would not be a consideration since finely divided material would permit of a quicker and more complete reaction and coarse material could readily be reduced to a finer condition.

The production of sugars and ethyl alcohol from

cellulosic materials such as straw, linen, cotton, peat and wood, in fact, all plant fibers, has engaged the attention of chemists and technologists for nearly a century, although it is only within the last two decades that serious attempts have been made to utilize wood waste by this means.

The principal sources of fermentable sugars from which alcohol is derived at present are:

1—Hydrolytic products of starch.

2—Sugars from fruits; sugar factory residues, such as molasses, etc

The cost of the raw material for alcohol derived from such sources, however, has been so high that alcohol had not been able to compete in certain fields where its properties and worth are recognized. The technical application in the arts and industries is gradually increasing, due to a rather liberal denaturing policy which has permitted special denaturants for special industries, but its use in this country as a source of liquid fuel is comparatively limited and it is this field that offers greatest possibilities in the future. A study of the motor fuel problem will show that the production of mineral fuels such as gasoline, motor spirits, etc., is not keeping pace with modern automobile production, and alcohol appears to be the only solution of the problem, for if alcohol can be produced from wood waste at a reasonable figure a tremendous supply of raw material is not only available at present but will continue to be so in the future from a natural growing raw material which is not a foodstuff.

#### PROCESS

The process of producing ethyl alcohol from wood consists, in general, of digesting sawdust or hogged and shredded wood with a dilute mineral acid at from 60 pounds and more of steam pressure. This converts part of the wood into a mixture of pentose and hexose sugars. The latter are then fermented, producing alcohol.

The processes using concentrated sulfuric acid, in which the wood is really attacked and dissolved by the acid as in the Ekström<sup>1</sup> process, have not received commercial attention, notwithstanding the fact that Flechsig,<sup>2</sup> many years ago, showed that cotton cellulose could be converted into dextrose and alcohol almost quantitatively thereby. The more recent work of Willstätter<sup>3</sup> and Feichmeister has confirmed these results with fuming hydrochloric acid, but in all cases the amounts of acid have been so large compared to the processes in which the acid is used merely as a catalytic agent, that the large initial and recovery costs for acid have prevented commercial development.

The source of the fermentable sugar, that is, whether derived from the cellulose or lignin of the wood, has long been a mooted question and has been the occasion of considerable investigation, but the fact remains that a wood cellulose like soda or sulfite pulp will produce about twice as much fermentable sugar and

<sup>1</sup> French Patent 380,358. German Patents 193,112, 207,354.

<sup>2</sup> *Z. phys. Chem.*, **1882**.

<sup>3</sup> *Ber.*, **1913**, 2401

alcohol as the original wood, the yields being proportional to the cellulose content.

#### HISTORY

The earlier work in the field from the time of Braconnot in 1819 until the work of Simonsen<sup>1</sup> in 1898, although exceedingly interesting historically, may almost be disregarded so far as its scientific value is concerned. It contains many inaccurate and impossible statements, and many contradictions, and is in many cases very vague in regard to yields.

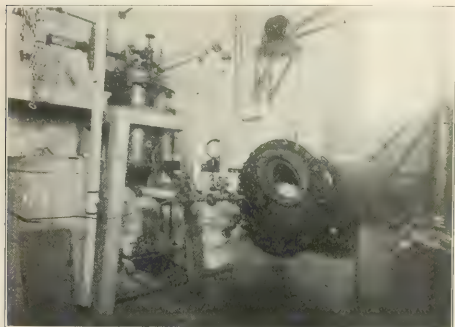


PLATE I—EXPERIMENTAL ALCOHOL APPARATUS

Showing digester with both manhole covers off, loaded with sawdust, and also tank T containing condensing coil and acid tank C.

Simonsen carried out the first systematic investigation of the subject in which the effect of different variables such as the amount of water, pressure, temperature, amount of acid, and time of inversion were studied in some detail. As shown later<sup>2</sup> by Neumann, Simonsen's work is also contradictory in some cases, due mainly to the fact that only a single experiment under each set of conditions was made. In his work on a large scale he was in general unable to duplicate the results obtained in the small autoclave cooks. The yields of alcohol varied considerably, although under the most favorable conditions he obtained in a few exceptional cases yields which were higher than those obtained on the small scale (6 per cent of dry weight of sawdust).

Since Simonsen published his work and took out patents on his process practically all over the world, the production of ethyl alcohol from sawdust has received considerable attention and a large amount of money has been spent in its technical development. Four plants have been built in this country, but none of them up to the present are considered to have achieved commercial success.

#### OUTLINE OF EXPERIMENTAL WORK

Although other investigators have duplicated Simonsen's yield, which is about six per cent by weight in alcohol of the dry weight of the wood, no systematic study has been made reinvestigating the variables studied by Simonsen, except the work of Cohoe in

<sup>1</sup> See E. Simonsen, *Zeitschrift für angewandte Chemie*, 1898, 195, 962, 1007; Theor. Körner, *Ibid.*, 1908, 2353; Neumann, Dissertation, Dresden, 1910.

<sup>2</sup> Neumann, Dissertation, Dresden, 1910.

which hydrochloric acid was used as the catalytic agent instead of sulfuric.

The data to be presented in this paper are the result of the first part of a systematic study of the variables in this process carried on at the Forest Products Laboratory and cover the first two of the following:

- 1—The influence of pressure and temperatures of digestion.
- 2—Length of time of digestion.
- 3—Ratio of water to dry sawdust.
- 4—Concentration of catalyzing agent in the water.
- 5—Ratio of catalyzing agent to dry sawdust.
- 6—Size of the sawdust, hogged slabs, etc.
- 7—Effect of adding catalytic agent (acid) after preliminary heating of the wood.
- 8—Effect of varying amounts of bark in the sawdust, or, more specifically, tannins, etc.
- 9—Special chemical treatments other than acid catalysis or in addition to acid catalysis.
- 10—A study of the fermentation variables.
- 11—Steam consumption per ton of sawdust inverted.
- 12—Variations of yields from different species and mixtures.

#### EXPERIMENTAL APPARATUS AND PROCEDURE

The apparatus used and method of procedure in each experiment were as follows: A rotary digester



PLATE II—EXPERIMENTAL ALCOHOL APPARATUS

Showing leaching tank, L, the settling tanks S and S<sub>2</sub>, the single effect vacuum evaporator E, and the hydroextractor H, in the foreground

consisting of thin cast-iron inner shell lined with acid-proof enamel and an outer shell of steel, the two being separated by several inches from each other, was used for the digestions. The internal length of the inner



shell is about five feet, and the diameter about 2 $\frac{1}{2}$  feet, making a total capacity of about 22 cubic feet. Steam is admitted to the inner shell and space between the inner and outer shell simultaneously, the digester being similar to a steam-jacketed apparatus except that the inner shell is removable and can readily be taken out and replaced. After a cook has been completed the digester is blown off, the blow-off vapors being condensed in a quartz coil. A cast-iron tank also lined with acid-proof enamel is connected to the digester so that its contents may be introduced into the digester when the latter is under pressure. This tank is used for acid storage and mixing. The steam flows to the inner shell and space between the two shells through separate pipes; the one leading to the inner shell also connects with acid tank. All pipes in contact with acid liquor or acid vapor are enamel-lined and valves are of special bronze so as to reduce corrosion to a minimum and to avoid complications in fermentations due to the presence of iron, copper, and zinc salts.

The pressure is taken by means of a gauge protected from the acid vapors and temperatures are taken on a recording thermometer, the bulb of which projects into the sawdust in the digester.

The digester is filled and emptied through a pair of concentric manholes in the inner and outer shell. The usual procedure is to load the digester with sufficient sawdust to be equivalent to about 100 pounds of dry dust. The exact weight and moisture content are recorded. The diluted acid is then added, the manhole covers bolted on, steam admitted, and rotation begun. Before the temperature reaches 100° C., the air in the inner shell and space between the two shells is vented so as to get a more accurate gauge reading. The admission of steam is continued until the desired pressure is reached, after which the steam is throttled to maintain that pressure for the desired length of time.

At the completion of the latter (or, in cooks of 15 minutes or more, two or three minutes before the time was up) the rotation was stopped and the vapors were then blown off and condensed as rapidly as possible. The time of blow-off varied somewhat, depending on the pressure at which the cook was made and the total amount of liquid and sawdust in the digester. The condensing and cooling capacity of the coil was not equal to the demands placed upon it so that the blowing off of the digester took much longer than it should (about two hours from 7 to 8 atmospheres to atmospheric pressure).

The condensed blow-off was weighed and analyzed. The steam which condensed between the two shells was drained out and weighed. It was also tested qualitatively for dextrose to detect any leakage from the inner shell. The liquor in the inner shell was drained out. After as much of the liquor as would do so had drained off the digester was rotated so that the manholes were at the bottom and the sawdust was raked out. In the later experiments this sawdust was then centrifuged.

Both the digester liquor and treated sawdust were weighed and analyzed for acidity, total solids, dextrose, etc.

The treated sawdust was next placed in the leaching tank, where the remainder of the sugar was extracted from it with warm water. The liquor from the digester and leaching tank was then neutralized with calcium carbonate and allowed to settle. The clear liquor was then concentrated in a single effect vacuum evaporator to a concentration of 10 to 15 per cent sugar for fermentation. The liquors were usually saved until the concentrations from two or three runs were obtained. Where possible, these were divided into two or more parts and fermented with brewers' yeast under varying conditions.

## RESULTS

**SUGAR YIELDS**—Figs. 1, 2 and 3 show the effect on yield of varying the pressure and time of cooking. The curves give the yields in total sugar instead of alcohol since the fermentation end of the work is being taken up in detail at present and was not standardized at the time these experiments were made so as to give check results. The greatest variation on dupli-

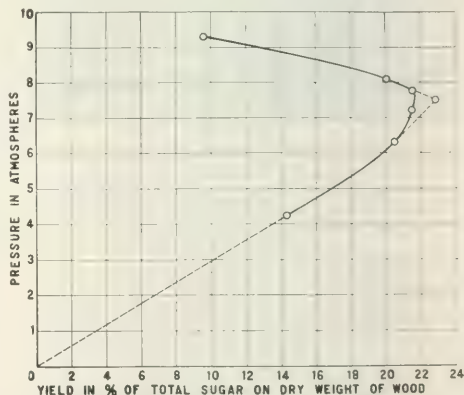


FIG. 1 SHOWING THE VARIATION OF YIELD OF TOTAL SUGAR WITH PRESSURE OF DIGESTION. COOKING PERIOD, 15 MINUTES

cate digestions made with sawdust from the same batch was only 0.11 per cent of total sugar, so the sugar data may be accepted as fairly accurate.

In each run the amount of sawdust used was very nearly equal to 100 pounds dry material; the amount of acid added was the same in all, 2.00 pounds of 90 to 95 per cent sulfuric; and the amount of water in all cases at the end of the cook was equal to four or more than four times the dry weight of wood used. The ratio of acid to dry wood was about 1.8 per cent, while that of water to dry wood was 400 per cent or more. Many of the charges were made up so that the initial amount of water present was exactly four times the dry weight of the material. These, however, showed no change from others in which the amount of water added was allowed to vary within certain limits.

Fig. 1, with a cooking period of 15 minutes, shows a decided maximum in yield at a temperature equal to 7.5 atmospheres steam pressure.

A new lot of sawdust was used for part of the work which included the cooks at 7.5 atmospheres and which

probably accounts for the increase in yields shown at that point and which has been indicated by the dotted lines.

On comparing the yields shown in Fig. 1 with those of Simonsen a much greater decrease in yields at pressures above 7.5 atmospheres was noted. From the work of Neumann it is known that dextrose decomposition is very rapid above  $175^{\circ}\text{C}.$ , which corresponds

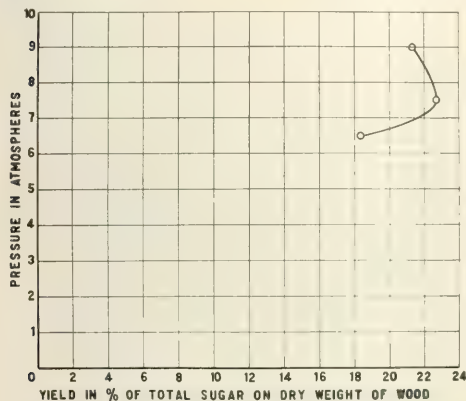


FIG. 2—SHOWING THE VARIATION OF YIELD OF TOTAL SUGAR WITH PRESSURE OF DIGESTION. COOKING PERIOD, ZERO MINUTES

very closely with 7.5 atmospheres pressure; in addition to this decomposition, however, the reaction seems to be reversible at this pressure, a fact which has not been recognized heretofore.

Fig. 2, with a cooking period of zero minutes (blowing off as soon as the pressure is reached), shows the same pronounced maximum at the same pressure and also shows a smaller decrease in yield at high pressures. Using the pressure of 7.5 atmospheres as a constant (at which the best yields were obtained as shown by

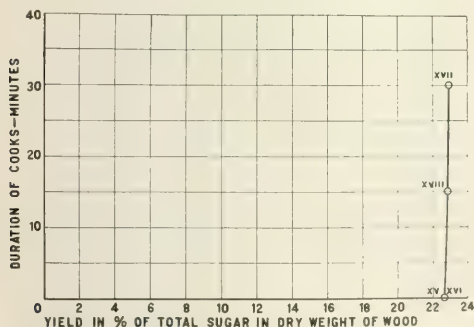


FIG. 3 SHOWING THE VARIATION OF YIELD OF TOTAL SUGAR WITH VARYING PERIODS OF DIGESTION. COOKING PRESSURE, 7.5 ATMOSPHERES

Figs. 1 and 2) and varying the time of cooking, as shown in Fig. 3, practically no increase or decrease in yield of sugar is shown; in other words, the rates of formation and decomposition of the sugars formed at this temperature are the same and, therefore, maintain a constant yield of sugar. At higher tempera-

tures, however, the rate of decomposition seems to be decidedly greater than the rate of formation which was shown in Figs. 1 and 2. In Fig. 1 the curve crosses the abscissae corresponding to 9 atmospheres at a point showing a yield of 14 per cent of sugar, while in Fig. 2 the yield of 9 atmospheres was 21.29 per cent of sugar. This decided difference in sugar values shows clearly the injurious effect of increasing the time of cooking, especially at pressures greater than 7.5 atmospheres.

The injurious effect of increased time of cooking is also shown in several other ways; the sawdust, of course, is rotated longer in the longer cooks and more fine stuff is formed which makes leaching and handling more difficult. The sawdust is also more friable and larger amounts of fine stuff were formed while being stirred in the leaching tank. And finally, as shown, by the ratio between sugar and total water-soluble solids, more of the sawdust was attacked so that the amount of extraneous water-soluble material other than sugars was greater.

Cohoe<sup>1</sup> was the first one to state that given the

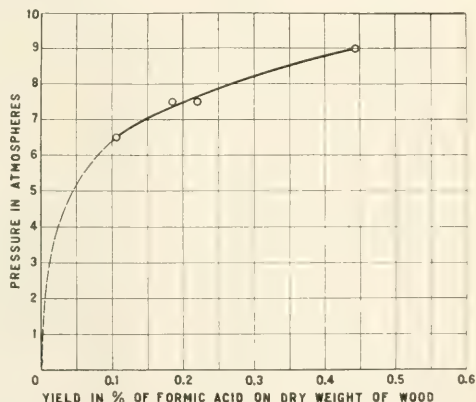


FIG. 4 SHOWING VARIATION OF FORMIC ACID YIELD WITH PRESSURE OF DIGESTION. COOKING PERIOD, ZERO MINUTES

proper adjustment of the various phases the reaction is practically instantaneous and our work is in entire agreement with this statement.

**VOLATILE ACID YIELDS**—In addition to the sugars formed as a result of hydrolysis, acetic and formic acid are also produced, probably from a splitting off of acetyl and formyl groups in the lignin complex. The yield of acetic acid has been fairly constant over a wide range of cooking conditions averaging 1.42 per cent of the dry weight of the wood. This is of particular interest not only because of its influence on the subsequent fermentation of the neutralized extract but also because it is practically the same yield obtained by destructive distillation of the wood. Numerous observers such as Klason, Büttner, and Wislicenus have shown that this decomposition does not take place until a temperature of  $280^{\circ}\text{C}.$  or more has been reached, whereas the temperatures of hy-

<sup>1</sup> Jour. Soc. Chem. Ind., 1912, 513

hydrolysis in this work have averaged 100° C. less than that. The yield obtained, however, is in very close agreement with the work of Bergström,<sup>1</sup> although the latter used no acid, merely hydrolyzing with 4 parts by weight of water at 6 atmospheres pressure for two hours.

The yield of formic acid, however, varies with the cooking conditions as shown by Fig. 4, the amount increasing with increasing cooking pressures. Increasing the time of cooking also materially increases the yield, for as shown at 7½ atmospheres and a zero-minute cook the yield is about 0.2 per cent, while at the same pressure for a 15-minute cook the yield is about three times as great (0.58 per cent). This increase in formic acid production also shows the rate of sugar decomposition since formic acid and levulinic acid are both products of such decomposition. The exact amount hydrolyzed from the wood is difficult to determine since it is also a product of sugar decomposition. Bergström obtained 0.19 per cent at 6 atmospheres cooking for two hours with water alone, whereas we have obtained that figure at 7½ atmospheres in zero minutes but only 0.105 per cent at 6.5 atmospheres in zero minutes. Technically, the yield of formic acid is of importance because of its influence on yeast growth.

Numerous patents granted in this field have discussed the value and recovery of the volatile acids produced. To show the distribution of the various acids, the amounts actually contained in the liquor drained from the inner shell, the condensed blow-off and moist sawdust, were calculated in percentages of the total amount of each acid produced. The results are given in the following table:

Cook number	PERCENTAGE OF TOTAL VOLATILE ACID IN						Total amt. of volatile acids in per cent of dry weight of original wood	
	Inner shell liquor	Condensed blow-off	Moist digested sawdust	Acetic	Formic	Acetic	Formic	Formic
XV.....	62.0	62.1	3.6	2.1	35.4	35.8	1.22	0.185
XVI.....	48.5	49.4	5.7	5.9	45.8	44.7	1.62	0.220
XVII.....	37.8	41.0	9.5	4.3	52.7	54.7	1.48	0.570
XVIII.....	40.2	46.2	7.2	7.0	52.6	46.8	1.32	0.598
XIX.....	35.0	32.6	6.8	6.1	58.2	61.3	1.60	0.443
XX.....	49.5	39.2	6.3	5.9	44.2	54.9	1.25	0.105

The average amount of acetic acid recovered in the blow-off was 6.4 per cent of the total, and 5.2 per cent of the total amount of formic acid produced.

With an average yield of 1.42 per cent of acetic acid, this would be equivalent to 1.81 pounds of acetic acid per dry ton of wood and since the average concentration of acetic acid in the condensed blow-off was only 0.20 per cent, commercial recovery is obviously out of the question.

**ALCOHOL YIELDS**—As mentioned heretofore, the fermentation work on the experiments outlined in this paper had not been standardized. Ordinary brewers' yeast, a bottom yeast, has been used without attempting to acclimate it to the mashies used. The main difficulty encountered was the slowness of fermentation which, in some cases, permitted infection of the mashies with wild growth. It was found, however, that the latter could be controlled and excluded by judicious sulfiting and for this purpose potassium

metabisulfite<sup>1</sup> was used. Various forms of organic and inorganic nitrogen nutrients were used, of which freshly killed yeast (boiling for two minutes in part of the mash) and ammonium nitrate proved to be the best.

The following table gives part of the results obtained:

Cook number	Total reducing sugars per cent of original dry wood	Per cent of total sugars fermented	Fermentation efficiency	Yield of alcohol per cent by weight of original dry wood	Yield of alcohol per U. S. gallons of absolute alcohol per dry ton of original wood
II.....	21.50	68.63	89.59	6.76	20.35
V.....	21.84	71.27	91.49	7.18	21.63
XVII.....	22.95	69.27	88.70	7.22	21.70
XVIII.....	22.85	53.5	96.2	6.24	18.75
XX.....	18.34	65.25	85.42	5.24	15.80
XIII.....	18.81	59.20	83.93	4.78	14.90
XIV.....	20.39	46.05	68.05	3.11	9.35
XII.....	11.58	55.24	68.87	2.25	6.8

Some of the above results, however, do not represent the yields obtainable under ideal conditions since many of the fermentations were retarded or spoiled entirely due to experimentation on fermentation conditions.

Under improved conditions with a yeast specially propagated the yields undoubtedly could be materially increased.

#### SUMMARY

I—The maximum yield of sugar was obtained at a pressure of 7.5 atmospheres and above and below this point yields decreased very rapidly.

II—A cooking period of zero minutes, that is, blowing off from 7.5 atmospheres as soon as that pressure is attained, was the most advantageous for sawdust.

III—Increasing the time of cooking did not increase the yield and greatly influenced the mechanical condition of the sawdust with greater subsequent difficulty and cost of handling. Economically speaking, the yield decreased as the time of cooking increased.

IV—Using white spruce sawdust as a raw material, from 22 to 23 per cent of the dry weight of the wood was converted into sugar. About 70 per cent of this sugar was fermented with an alcohol yield of over 91 per cent of the amount theoretically possible to obtain from the fermentable sugars. Calculating these yields to a tonnage basis, between 21.63 and 21.70 U. S. gallons of absolute alcohol were obtained per dry ton.

V—Under a rather wide range and variation of cooking conditions of hydrolysis, white spruce yielded about 1.4 per cent acetic acid, showing, therefore, a parent substance (lignin?) of a comparatively definite acetyl content.

VI—The yield of formic acid varied with the conditions of hydrolysis. In cooks longer than zero time, the formic acid yield was indicative of hexose decomposition rather than increased formyl hydrolysis.

FOREST PRODUCTS LABORATORY  
FOREST SERVICE, U. S. DEPARTMENT OF AGRICULTURE  
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MADISON

<sup>1</sup> See "Enological Investigations," F. T. Bioletti and W. V. Cruess, *Bull.* 230, Agr. Expt. Sta., Berkeley, Cal.



# THE OIL OF PORT ORFORD CEDAR WOOD AND SOME OBSERVATIONS ON *d*- $\alpha$ -PINENE

By A. W. SCHORGER

Received May 4, 1914

The Port Orford cedar [*Chamaecyparis lawsoniana* (Murr.) *Parlatore*] occupies a very restricted range. It is found along the Pacific coastal region from Coos Bay in southwestern Oregon to the Mad River in northwestern California. The wood contains an oil having a strong, pleasant odor, and a pronounced physiological action on the kidneys. Owing to the effect of the inhaled vapors upon the workmen, mills cutting Port Orford cedar do not operate continuously on this species.

Selected "resinous" pieces of wood on steam distillation yielded 10 per cent of oil having  $d_{15}^0$  0.891,  $n_{D15}^0$  1.477. On distillation, a blood-red residue remained in the distilling flask. (The distiller of this oil was physiologically affected in the usual way.)

The oil when it reached the author was *four years* old and had been stored in a tightly stoppered amber-colored bottle. The constants were redetermined with the following results:  $d_{15}^0$  0.9061,  $n_{D15}^0$  1.4806. The oil was rectified by shaking with 10 per cent  $\text{Na}_2\text{CO}_3$  solution and distilling with steam over soda solution. By this treatment the oil lost 16.4 per cent by volume. In the subsequent examinations of the oil no physiological effects were noted and no red residue on distillation. It is possible that the cause of both phenomena was destroyed by aging.

## EXPERIMENTAL

The rectified oil had the following constants:  $d_{15}^0$  0.8905;  $n_{D15}^0$  1.4758;  $\alpha_{D25}^0$  +39.60°; acid no. 0.30; ester no. 32.8; ester no. after acetylation 71.57. The ester numbers before and after acetylation are equivalent to 11.48 per cent bornyl acetate and 10.00 per cent of free borneol. The oil distilled as follows: 155–157°, 60.5 per cent; 157–170°, 3 per cent; 170–180°, 4 per cent; 100–130° at 15 mm., 20.5 per cent; 130–160° at 15 mm., 7 per cent; 160–190° at 15 mm., 1 per cent. When distilled at normal pressure decomposition took place above 180° with the splitting off of acetic acid.

$\alpha$ -PINENE—Preliminary examination of the  $\alpha$ -pinene fractions indicated that this terpene was present in an exceptionally pure state for a natural product. By fractionation over sodium 65 per cent of the  $\alpha$ -pinene fraction was obtained in a pure state. The carefully determined constants were as follows: B. p. 156.0–156.1 (760 mm.);  $d_{15}^0$  0.8631;  $n_{D15}^0$  1.4684; specific rotation  $[\alpha]_D^{25}$  +51.52°. The molecular refraction was found to be  $M = 43.88$ ; calculated for  $\text{C}_{10}\text{H}_{16}$   $\overline{M}$ , 43.54. The highest previously recorded specific rotations for  $\alpha$ -pinene are:  $[\alpha]_D^{25}$  +48.4° for *d*- $\alpha$ -pinene from Grecian turpentine oil;<sup>1</sup>  $[\alpha]_{D19}^{25}$  –48.63° for *l*- $\alpha$ -pinene from silver-top stringy-bark eucalyptus oil (*Eucalyptus laevopinea*).<sup>2</sup>

Ten grams of the  $\alpha$ -pinene fraction did not yield a trace of crystalline pinene nitroschloride. One hundred grams of the terpene were then oxidized with

233 grams  $\text{KMnO}_4$  in 1.5 liters of water and 500 grams of ice in an ice bath. On completion of the oxidation 25.3 grams of oil were recovered by steam distillation. The recovered oil after standing a week deposited a few fan-shaped clusters of needles. This product was evidently pinol hydrate, since it melted at 144–145° after one crystallization from water. After removal of the manganese sludge the oxidation liquor was evaporated to one liter and extracted several times with ether. The pinonic acid precipitated by dilute sulfuric acid was extracted with chloroform and the solvent removed by distillation. The residue distilled between 185–190° at 17 mm., mainly between 187–188°. The distillate weighing 34.8 grams soon crystallized on standing and 16.6 grams of the crystalline keto-acid were obtained. The crystalline *d*-pinonic acid melted at 68–69°, its semicarbazone at 203–205°. The specific rotation of the acid  $[\alpha]_D^{25}$  +92.69° was determined from a 5.37 per cent chloroform solution. The semicarbazone of the liquid pinonic acid melted at 203°.

DIPENTENE—The fractions, b. p. 157–180°, consisted mainly of dipentene. The portion, b. p. 170–180°, comprising the major portion of the oil had a rotation  $\alpha_{D25}^0$  +51.16°. Phellandrene was not detected and the dihydrochloride from this fraction melted at 48–49°. On bromination a tetrabromide melting at 124° was obtained. The high rotation indicates the presence of active limonene.

BORNEOL—The free alcohol obtained by saponification of the fraction, b. p. 100–130°, at 15 mm. distilled between 205–230° and was collected in 5° fractions. By oxidation with acetic and chromic acids on the water bath camphor could be detected in each fraction. The oxidation products were oils with a strong camphor odor. On treatment with semicarbazide hydrochloride, crystalline semi-carbazones were obtained, melting at 236–237°. However, by oxidizing the oil, b. p. 205–215°,  $\alpha_{D20}^0$  +32.16, with saturated permanganate solution and distilling with steam, solid camphor collected in the receiver. An alcoholic solution of the camphor was *d*-rotatory.

COMBINED ACIDS—The combined acids were recovered from the ester saponification liquor by distillation with phosphoric acid. A small amount of oily material appearing on the surface of the distillate was removed by extraction with ether. The solvent was allowed to evaporate spontaneously, the residue neutralized with caustic soda and extracted with ether, to remove resinous matter. On addition of  $\text{AgNO}_3$  solution a precipitate was obtained and analyzed as follows:

0.0814 gram silver salt gave 0.0313 gram  $\text{Ag} = 38.45$  per cent  $\text{Ag}$ .

Silver capricate,  $\text{C}_{18}\text{H}_{36}\text{COOAg}$ , requires 38.66 per cent  $\text{Ag}$ .

The acids in the aqueous portion of the distillate were neutralized with caustic soda and precipitated with silver nitrate. The precipitates were found to contain silver formate, as shown by the decomposition on attempting to recrystallize them from hot water. The silver formate was accordingly destroyed by alternate

<sup>1</sup> Vezes, *Bull. soc. chim.*, [4] 5 (1909), 932.

<sup>2</sup> Smith, *Jour. and Proc. Royal Soc.*, N. S. W., 32 (1898), 195.

heating and filtration of the aqueous solution until decomposition had ceased. The shiny leaflets of silver acetate finally obtained were analyzed as follows:

0.1245 gram silver salt gave 0.0802 gram Ag = 64.42 per cent Ag.

Silver acetate,  $\text{CH}_3\text{COOAg}$ , requires 64.64 per cent Ag.

**FREE ACIDS**—The acids recovered from the liquors remaining after rectifying the oil with sodium carbonate solution and steam distillation were treated as above. The acid obtained from the other extract was precipitated in two fractions and their silver content determined:

(1) 0.0621 gram silver salt gave 0.0241 gram Ag = 38.81 per cent Ag.

(2) 0.0836 gram silver salt gave 0.0325 gram Ag = 38.87 per cent Ag.

Both precipitates evidently consist of silver caprinates since this salt requires 38.66 per cent Ag.

The aqueous portion was found to consist of acetic and formic acids. In this case the formic acid was destroyed by heating the distillate with mercuric oxide. Analysis of the silver salt of the remaining acid follows:

0.1993 gram silver salt gave 0.1283 gram Ag = 64.38 per cent Ag.

**CADINENE**—The fractions boiling above  $130^\circ$  at 15 mm. contained cadinene. The portion, b. p.  $270-280^\circ$ ,  $d_{40}^{20} 0.9329$ ,  $\alpha_{D_{20}} +14.60$ , yielded the characteristic cadinene dihydrochloride, m. p.  $117-118^\circ$ . A 6.04 per cent ether solution of the dihydrochloride had the rotation  $\alpha_{D_{20}} -1.05^\circ$ .

#### SUMMARY

The rectified oil has approximately the following composition: *d*- $\alpha$ -pinene 60-61 per cent; dipentene 6-7 per cent; free *l*-borneol 11 per cent; ester as bornyl acetate 11.5 per cent; cadinene 6-7 per cent; losses 5 per cent. The combined borneol occurs mainly as bornyl acetate, but also evidently as the esters of formic and capric acids. In the old oil, formic, acetic, and capric acids occur in the free state.

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FOREST SERVICE, U. S. DEPARTMENT OF AGRICULTURE  
(In Cooperation with the University of Wisconsin)  
MADISON

#### THE RELATION BETWEEN ALUMINUM SULFATE AND COLOR IN MECHANICAL FILTRATION<sup>1</sup>

By FRANK E. HALE

The older literature, especially the English, frequently speaks of the humic acid of swamp waters, particularly in connection with the solution of lead by drinking water. In recent years the tendency has been to consider free acidity due to carbonic acid and to be rather skeptical of the existence of free organic acid in water. The experiments described in this paper seem to prove that free organic acid in water is no myth, but actually exists as a property of the coloring matter, and in all probability the removal of color by the action of aluminum sulfate depends upon this acid property. The acid coloring matter combines with the base, aluminum hydrate, and in definite

proportions, the ratio varying with the chemical character of the color in different waters.

This theory is in keeping with the fact that practically all organic coloring matter extracted from wood or vegetable growth combines with almost any hydrate, *e. g.*, tin, bismuth, aluminum, chromium, iron, etc. Recently, at Grand Rapids, Mich., in the softening of water, it has been found that excellent decolorization is obtained by means of an excess of magnesium hydrate.<sup>1</sup>

#### THE REACTION BETWEEN ALUMINUM SULFATE AND THE ALKALINITY

It is usually stated that this reaction results in the formation of aluminum hydrate,  $\text{Al}(\text{OH})_3$ . In elementary courses in chemistry it is taught that the reaction between aluminum salts and sodium carbonate results in the cold in the precipitation of basic aluminum carbonate, which only upon boiling changes completely to the hydrate. This is undoubtedly the reaction occurring in water between aluminum sulfate and calcium bicarbonate. Indeed, judging from the amount of alkalinity reacting with one grain per gallon of basic aluminum sulfate and from the amount of carbonic acid set free, there is good reason to believe that the precipitate formed is a basic sulfate-carbonate.

The usual aluminum sulfate employed is a basic salt containing about 18 per cent alumina ( $\text{Al}_2\text{O}_3$ ). The analyses of seventeen samples, representing several years, of the aluminum sulfate used at the Brooklyn filters were as follows:

Percentages	$\text{Al}_2\text{O}_3$	$\text{SO}_3$
Average ..	18.2	39.3
Minimum ..	16.6	35.9
Maximum ..	20.6	41.4

The sulfate varied from a few per cent to twenty per cent below the amount theoretically required by the alumina to form a neutral salt. The average deficiency was 11 per cent. This average salt may be expressed by the formula  $\text{Al}_2(\text{SO}_4)_3 \cdot \text{Al}(\text{SO}_4)(\text{OH})$ , but I prefer the doubled formula  $2\text{Al}_2(\text{SO}_4)_3 \cdot \text{Al}_2(\text{SO}_4)_2(\text{OH})_2$ , since when written graphically it better explains the probable reactions with the alkalinity. Theoretically an aluminum sulfate containing 18 per cent alumina requires 9 p. p. m. calcium carbonate to react completely, thus:

P p m alkalinity =  $300 \times 102 \times 17.1 \times 18 \div 100 = 9$   
in which 300 is the molecular weight of  $3\text{CaCO}_3$   
102 is the molecular weight of  $\text{Al}_2\text{O}_3$   
17.1 is the p. p. m. equivalent of 1 grain per gallon  
18 is the per cent of alumina

But it is not the alumina that combines with the alkalinity. It is the sulfate. As the sulfate is 11 per cent short in the average aluminum sulfate the maximum alkalinity that can react with the average coagulant is 8.3 p. p. m. It will vary with the actual composition and is also governed by other conditions such as a low or a high alkalinity, and a low or a high turbidity. With a high alkalinity the figures approach the upper limit but with a low alkalinity they fall short, even as low as 5.5; in fact figures have been published as low as 3.4, using alum containing 18 to 22 per cent alumina. The following table gives some of the figures found in practice:

<sup>1</sup> Presented at the 49th Meeting of the A. C. S. Cincinnati, April 6-10, 1914.

<sup>1</sup> "Report of Committee on Water Supplies," *Am. Jour. Pub. Health*, 3 (1913), 1335.

LOCATION	Years	Color	Alkalinity	Alum. grains per gallon	Alkalinity reacting with 1 gr. per gal. of alum.
Louisville Water Co. (a).....	1912	2	55	1.18	8.5
Elmira Water Works (b).....	1907	20	52	1.55	7.4
Springfield, Mass. (a).....	1912	40	8	0.27	7.3
Little Falls, N. Y. (a).....	5 months	41	28	1.30	7.1
Rensselaer, N. Y. (b).....	1901-1908	25-65	18-65	2.04	6.8
Harrisburg, Pa. (b).....	1906	17	27	0.95	6.4
Harrisburg, Pa. (b).....	1907	13	25	1.06	6.2
Harrisburg, Pa. (a).....	1910	4	49	0.61	5.4
Harrisburg, Pa. (a).....	1911	7	29	0.7	6.6
Croton water, N. Y. City (c).....	1912	25	35	1.0	6.2
Brooklyn water, N. Y. City (c).....	1912	5	12	1.0	6.0
Baileys Filter, Brooklyn.....	1907	30	31	1.69	5.8
Norwich, N. Y. (b).....	1905-1908	12	20	0.34	5.6
General average.....					6.6
(a) Reports.					
(b) J. A. Caird, <i>Proc. Am. W. W. Assoc.</i> , 1908, p. 371.					
(c) Laboratory experiments.					

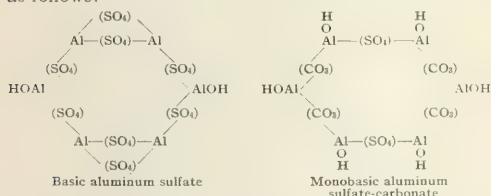
In many careful experiments I have found an average of 3.5 p. m. carbonic acid set free by one grain per gallon of basic aluminum sulfate reacting with the bicarbonates of natural waters. This is also about the usual figure obtained at Little Falls (information obtained from Mr. Geo. W. Fuller, Consulting Engineer).

Basing a reaction upon an average figure of one grain per gallon of aluminum sulfate (11 per cent basic) reacting with six alkalinity and setting free 3.5 p. m. carbonic acid, the following equation may be written:

$$2\text{Al}_2(\text{SO}_4)_3 \cdot \text{Al}_2(\text{SO}_4)_2(\text{OH})_2 + 6(\text{CaCO}_3 \cdot \text{H}_2\text{CO}_3) + 4\text{H}_2\text{O} = 2\text{Al}_2(\text{CO}_3)_2(\text{OH})_2 \cdot \text{Al}_2(\text{SO}_4)_2(\text{OH})_2 + 6\text{CaSO}_4 + 8\text{H}_2\text{CO}_3$$

In this equation the carbonate reacts only with the neutral sulfate to form a monobasic carbonate. The basic sulfate portion of the salt does not react. With waters of high alkalinity probably all of the sulfate is changed to carbonate.

These salts may be represented graphically in part as follows:



It may be conceived that all of the sulfate is replaced by carbonate except where there are two sulfate radicles between two aluminum atoms, where only one is replaced. A strain is thus produced at this point, the carbonate hydrolyzes and the result is a hydroxyl radicle attached to each aluminum atom. With high alkalinity, that is, a large excess of carbonate, the remaining sulfate radicles become replaced.

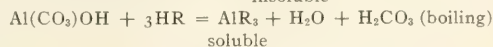
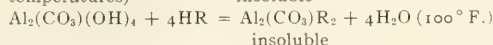
#### THE REACTION BETWEEN THE COLOR AND THE ALUMINUM SALTS

The acid coloring matter combines with the hydroxyl radicles of the above and is removed from solution only because of the insolubility of the carbonate of aluminum.

The above reactions take place at ordinary tempera-

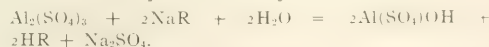
tures. Mr. G. C. Whipple<sup>1</sup> in a comprehensive discussion of decolorization of water (page 161) gives a table in which 1.2 grains per gallon of aluminum sulfate were required to decolorize a water of 50 color at 44° F., and 0.8 grains at 98° F. This is probably due to the formation of a dibasic aluminum carbonate  $[\text{Al}_2(\text{CO}_3)(\text{OH})_4]$  so that the same amount of aluminum sulfate can react with twice the amount of color. At boiling temperature, however, when  $\text{Al}(\text{OH})_3$  is formed I have found that 3 grains per gallon of aluminum sulfate did not reduce a color of 90 but intensified it to 130, although the same amount in cold reaction reduced the color to 36. I believe this must be due to the formation of a compound in which the aluminum is entirely combined with the coloring matter and that this compound is soluble. This would explain the fact that as the color of a water increases it requires more aluminum sulfate to reach the starting point of the precipitation and color removal, the excess color at first having a solvent action. This is in line with the fact that iron in combination with coloring matter is soluble.

The reactions may be represented as follows, letting HR represent the coloring matter and ignoring the complex combinations when sulfate does not completely react:



Likewise  $\text{Al}(\text{OH})_2\text{R}$  and  $\text{Al}(\text{OH})\text{R}_2$  should be insoluble.

On pages 156 to 159 (previous citation), Mr. Whipple discusses a direct reaction between aluminum sulfate and coloring matter in the absence of all alkalinity and on page 157 gives a chart showing greater color removal for the same amount of alum. It must be borne in mind, however, that aluminum sulfate acts as a dilute acid upon color, changes it to a greenish hue and lightens it as any acid will, so that the effect of color removal is heightened. If the color be neutralized again the apparent color at the end is about doubled. There is, however, a direct reaction, as shown by the formation of a precipitate whether aluminum sulfate is added to a neutral water or added in excess to an alkaline water. It is probable that not all of the color is of acid character and if such color is represented by NaR the reaction with aluminum sulfate to acidify the color may be written:



The precipitation and decolorization may be written:

$$\text{Al}_2(\text{SO}_4)_3 + 6\text{NaR} + 2\text{H}_2\text{O} = 2\text{Al}(\text{OH})\text{R}_2 + 3\text{Na}_2\text{SO}_4 + 2\text{HR}$$

insoluble

residual color

It will be noted that this equation requires a residual color one-third the original color. Mr. Whipple states, on page 161 (previous citation), that such resid-

<sup>1</sup> *Trans. Am. Soc. Civil Eng.*, 46 (1901), 141-181.



usual color usually resulted, as much as 50 in one case of 300 original color. As he used 6.5 grains per gallon of aluminum sulfate, this reaction was probably an excess alum reaction, the color would be acid in character and would represent about 100 original color neutral, or one-third of the original total color if that were all neutral. In my experiments, to be described later, the Great Swamp water neutralized had a color of about 200. In the acid treatment with excess aluminum sulfate the residual color was 25, representing when neutralized 50 p. p. m. or one-fourth the original color neutralized.

During the last two years this acid reaction has had practical application at Springfield, Mass.<sup>1</sup> The supply has been treated with excess aluminum sulfate for a definite period and then allowed to mix and react with untreated supply for another definite period. The results for 1912 are summarized in the following table:

Month	Color orig. P. p. m.		Reduction in color P. p. m.		Alkalinity original P. p. m.		Reduction in alk. P. p. m.		Alum. suff. Grs. per gal.		Reduction per one gr. per gal. alum.	
	Color	Alk.	Color	Alk.	Color	Alk.	Color	Alk.	Color	Alk.	Color	Alk.
Jan. (a)	32	17	7	5	1	6	0	19	89	8.4		
Feb. (a)	37	24	8	0				29	83			
Mar.	33	20	6	8	1	1	0	21	95	5.2		
Apr.	34	21	6	4	1	3	0	22	95	6.8		
May	38	25	8	1	1	9	0	25	100	7.6		
June	38	21	11	0	2	5	0	25	84	10.0		
July	38	21	9	6	1	4	0	20	105	7.0		
Aug.	36	19	9	5	1	9	0	19	100	10.0		
Sept.	42	25	10	3	1	6	0	26	96	6.2		
Oct.	50	32	9	3	1	2	0	27	119	4.4		
Nov.	58	40	7	8	3	9	0	58	69	6.7		
Dec.	46	31	6	5	3	2	0	38	82	8.4		
Average	40	25	8	4	2	0	0	27	93	7.3		

(a) Days included only when alum was used.

It will be noted that double the usual amount of color has been removed per grain per gallon of aluminum sulfate. The probable reason for this rests in the reactions already given and there is probably produced a mixture of  $AlR_2OH$  and  $Al(CO_3)R$  and possibly  $Al_2(CO_3)R_4$ . The acidifying effect of the aluminum sulfate upon the neutral coloring matter renders it more active and at the same time tends to produce apparently an aluminum precipitate containing twice the amount of color that is combined in the usual cold reaction.

With waters of a high alkalinity a greater amount of aluminum sulfate is required to decolorize a water by the usual method than in a water of low alkalinity. This is probably due to a solvent effect of the alkalinity by a tendency to form alkaline aluminates and in fact precipitation will not take place in many cases until sufficient alum is added to neutralize the excess alkalinity. I have noticed this especially in trade wastes and it was noted at New Orleans with a natural water.<sup>2</sup>

It might be advisable to call attention also to an article on "Hot Water Problems,"<sup>3</sup> in which considerable space is given to color discussion by Mr. G. C. Whipple, since it does not appear in the title.

<sup>1</sup> Eng. News, 70, Nov. (1913), 974; Am. Jour. Pub. Health, 3, 1333.

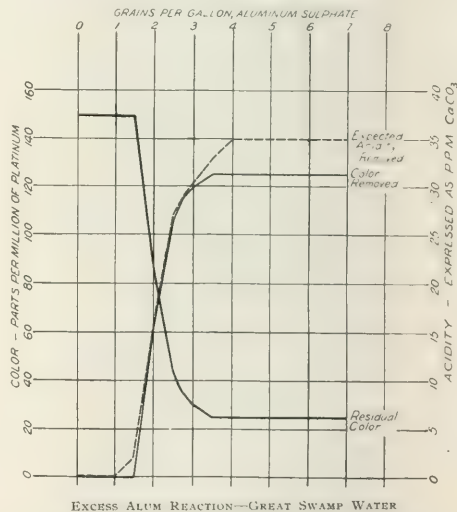
<sup>2</sup> Trans. Am. Soc. Chem. Eng., 46 (1901), 168.

<sup>3</sup> Proc. Am. W. W. Assoc., 1911, pp. 261-276.

## THE ACIDITY OF COLORING MATTER IN NATURAL WATERS

These experiments were performed upon the Great Swamp water of the south and upon Charleston, S. C., water.

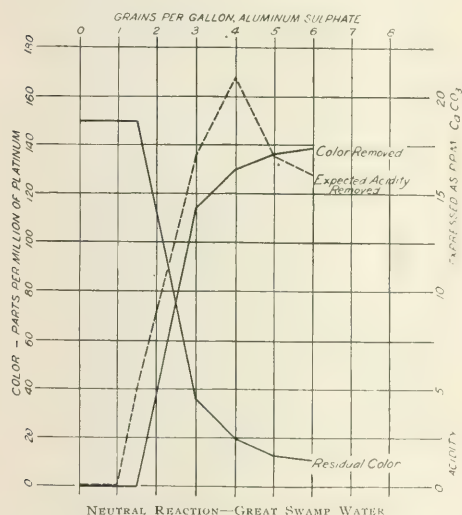
The Great Swamp water had an alkalinity of 9 p. p. m. and a color of 150 p. p. m. Using 200 cc. portions, varying amounts of aluminum sulfate solution were added, allowed to react for a definite period, usually one-half hour, and filtered through two layers of S. & S. No. 589 paper, previously washed twice with some of the water to be filtered. The amounts of aluminum sulfate added ranged from one to seven grains per gallon. The alkalinity of this water, on a basis of 6 p. p. m. alkalinity reacting with one grain per gallon, could react with 1.5 grains per gallon of alum. With this amount no apparent reaction took place. There was no precipitation and no reduction of color upon filtering. That there was a reaction with the alkalinity, however, was shown by an increase in free carbonic acid. Beginning with 1.75 grains per gallon, precipitation commenced and rapidly progressed to 2.5 grains, then slightly more color was removed up to 4 grains, when further reaction ceased with a residual



color of 25 p. p. m. This reaction of coloring matter in the presence of excess aluminum sulfate was practically the same phenomenon mentioned by Whipple and now practiced at Springfield, although at the time these experiments were performed I was not acquainted with this work and discovered the reaction by accident. I desire at this point to thank Mr. Geo. W. Fuller for calling my attention to this work of Whipple and of Lockridge.

As the aluminum sulfate and the alkalinity react in colorless waters the free carbonic acid is increased, an average of 3.5 p. p. m. for each grain of alum per gallon, when 6 alkalinity reacts and the alum contains 18 per cent alumina, due to the setting free of bicarbonic acid and a small part of the neutral carbonate.

The equation for this reaction was given in connection with the graphic formulae. With the highly colored Great Swamp water the theoretical increase of acidity was produced up to 1.5 grains per gallon of alum while *no color was being removed*, but as the color was removed a certain amount of the expected increase of acidity failed to appear and just in proportion to the amount of color removed. After the removal of color stopped, the theoretical increase of acidity commenced again. The accompanying tables and charts show this strikingly. The expected increase of acidity after the alkalinity was used up was due to the excess of aluminum sulfate added. The acidity removed from the solution in the above reaction was undoubtedly due to the removal of acid coloring matter with possibly a small amount of included alum. Titration of the filtrate with *N*/50 sodium carbonate using lacmoid and boiling indicated about one and two-thirds grains per gallon of aluminum sulfate reacting and removed from the solution as against one and one-half theoretical.



The above experiments were repeated adding as exactly as possible neutral sodium carbonate solution (*N*/50) to supplement the alkalinity. Again the expected increase of acidity was reduced directly proportional to the amount of color removed, but the lost acid was only about one-half the quantity of acid removed in the previous experiment. This was undoubtedly due to the removal of acid in the coloring matter only since the excess of aluminum sulfate was neutralized by the sodium carbonate. The color removal in neutral solution was again very rapid between 1.5 and 3 grains per gallon of alum and progressed slowly up to 7 grains, at which only a color of 9 p. p. m. was left.

About 40 p. p. m. color were removed per grain of aluminum sulfate per gallon and about 7 p. p. m. color possessed 1 p. p. m. acidity, expressed as  $\text{CaCO}_3$ .

The water of Charleston, S. C., possessing an alkalinity of 15 p. p. m. and a color of 80, was tried in the same way with similar results, the removal of expected acidity proportional to the removal of color. With this water about 30 p. p. m. color were removed per grain of aluminum sulfate per gallon and 5 p. p. m. color possessed 1 p. p. m. acidity.

It is interesting and important to note also that the amounts of color removed in these two waters bear a relation to the acidity, *e. g.*, 30 : 40 = 5 : 7.

Several other experiments appear to confirm the existence of free organic acid in natural waters. Free carbonic acid may be removed from water by blowing air through it or by boiling. The Great Swamp water originally contained considerable free acid, but upon standing the free acid became greatly reduced to a point at which it became practically constant, 1.8 cc. *N*/50 sodium carbonate per 100 cc. water, equivalent to 18 expressed as  $\text{CaCO}_3$ . This residual acidity was probably due entirely to the coloring matter and agrees fairly well with the results obtained by loss of expected acidity upon removing the color, 17. Charleston water showed the same phenomenon, a residual acidity of 12 upon standing a long time, against a loss of expected acidity with removal of color of 10.

Upon aerating the Great Swamp water when it contained an acidity of 34, expressed as  $\text{CaCO}_3$ , for five minutes the residual acidity was 14 p. p. m., upon aerating for one hour 14, upon aerating for fifteen minutes with air drawn through lime water 14. Upon boiling one hour the acidity was reduced to 10, the boiling probably causing some change in the coloring matter.

Upon adding dilute acid to the water the color was greatly decreased and brought back by alkali. Upon adding alkali, sodium carbonate, to the original water the color was considerably increased. Upon neutralization Great Swamp water increased in color from 150 to 192. Upon adding 4 cc. excess of *N*/50 sodium carbonate the color became 212 and 8 cc. excess produced no further increase of color. To a portion treated with alum and soda in which the color had been reduced to 13, excess soda raised the color to 26.

Upon neutralizing exactly the residual free acidity of Charleston water probably due entirely to color, with either soda or lime water, 2 grains of alum per gallon reduced the color to only 68 and 70, respectively, although in the unneutralized water 2 grains reduced the color from 80 to 27 p. p. m. The setting of the color in presence of excess alkali, so that the color is more difficult to remove by alum, has been noted at New Orleans (local citation) and was noticed by the author during investigation of corrosion of iron pipes by water. This effect may be due to one or all of three causes: (1) Neutralization of the acidity of the color so that it does not properly react with the aluminum sulfate; (2) increase of color intensity by the neutralization; (3) formation of soluble alkaline aluminates.

It is well known that iron frequently exists in organic combination in water and in such condition is very difficult to remove. The author examined a series

of samples of water from northern New York state in which in some samples the color could not be reduced beyond about 15 p. p. m. even with a large excess of alum up to 5-7 grains per gallon. The residual unremovable color<sup>1</sup> in different samples was found to vary almost exactly with the iron content as follows:

Residual color	Iron p. p. m.
4	0.15
13	0.45
16	0.60

This may have been due to the combination of the iron with the acid radicle of some of the color so that it could not react with the alum. In this water also 1 grain per gallon of alum removed only 12 p. p. m. color and the precipitation did not take place until about two, three and four grains, respectively, were added. This water had an alkalinity of about 75 which also was probably partly responsible for the slow start of reaction.

The following tables and charts give the results of these experiments with Great Swamp water and Charleston water. In order to estimate correctly the expected acidity, experiments were made which showed that: (1) one grain per gallon of the aluminum sulfate used reduced the alkalinity 6 p. p. m., using either methyl orange or lacmoid (boiling) as indicator; (2) one grain per gallon of aluminum sulfate (11 per cent basic) reacting with calcium bicarbonate produced an acidity to phenolphthalein of 0.8 cc. *N*/50 sodium carbonate per 100 cc. of water, equal to 3.5 p. p. m. carbonic acid ( $\text{CO}_2$ ) or 8 expressed as  $\text{CaCO}_3$  p. p. m.; (3) one grain per gallon of aluminum sulfate in excess produced an acidity to phenolphthalein of 1.8 cc. *N*/50 sodium carbonate per 100 cc. of water or 18 expressed as  $\text{CaCO}_3$ . This last reaction may possibly be represented by the following equation:  $\text{Al}_2(\text{SO}_4)_3 + 8\text{Na}_2\text{CO}_3 + 4\text{H}_2\text{O} = 2\text{NaAlO}_2 + 4(\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{CO}_3) + 3\text{Na}_2\text{SO}_4$ .

This equation is equivalent to 1.6 cc. *N*/50 sodium carbonate per 100 cc. water when one grain per gallon of basic alum reacts with 6 alkalinity. The equation for neutral alum as expressed, calls for 2.4 cc. of the carbonate.

REACTION OF GREAT SWAMP WATER, ALKALINITY 9 P. P. M., WITH BASIC ALUMINUM SULFATE

Alum. sulf. per gal.	Color	P. p. m.	<i>N</i> /50 Na <sub>2</sub> CO <sub>3</sub> per 100 cc.	Theoretical increase in acidity	Theoretical total free acidity	Actual found	Expected acidity lost expressed as CaCO <sub>3</sub>	Reduction in color	Color equivalent to one acid	Color removed by 1 gr per gal alum
			Cc.	Cc.	Cc.	Cc.				
0	150	0.0	0	0	0	0	0	0	0	0
1	150	0.8	3.5	3.5	3.5	3.5	0	0	0	0
1.5	150	1.2	3.9	3.7	2	0	0	0	0	0
2	86	2.1	4.8	3.8	16	64	4	32	4	32
2.5	44	3.0	5.7	4.8	27	106	4	42	4	42
3	35	3.4	6.1	3.2	29	115	4	42	4	42
3.5	30	3.9	6.6	3.7	29	120	4	40	4	40
4	28	4.3	7.0	4.2	33	125	4	36	4	36
4.5	25	5.7	8.4	4.8	36	125	4	36	4	36
5	25	7.5	10.2	6.7	35	125	4	36	4	36
6	25	9.3	12.0	8.5	35	125	4	36	4	36
7	25	11.1	13.8	10.3	35	125	4	36	4	36

It was also assumed that one grain per gallon of aluminum sulfate reacting with neutral sodium carbonate formed a monobasic carbonate of aluminum in the precipitation and set free carbonic acid equivalent to 0.2 cc. *N*/50 sodium carbonate per 100 cc. of water.

<sup>1</sup> Page 161, local citation

Expected acidity up to 1.5 grains per gallon of alum was due to carbonic acid set free from 9 p. p. m. alkalinity, after that due to excess of alum.

The ratio of color to acid removal in this reaction differs from the following neutral reaction value and rightly since the excess alum turns the color greenish and lightens it by half. Therefore, the color equivalent to one acidity is about half that in the following table:

REACTION OF GREAT SWAMP WATER WITH BASIC ALUMINUM SULFATE—AND ADDED SODIUM CARBONATE TO PRODUCE JUST SUFFICIENT ALKALINITY FOR REACTION

Alum. sulf. per gal.	Soda N 50 per 100 cc.	Color	P. p. m.	Theor increase in acid	Theoretical total free acidity	Actual found	Expected acidity lost expressed as CaCO <sub>3</sub>	Reduction in color	Color equivalent to one acid	Color removed by 1 gr per gal alum
	Cc.	Cc.	Cc.	Cc.	Cc.	Cc.				
0	0	150	0.0	0.0	3.4	3.4	0	0	0	0
1.5	0.0	150	1.2	4.6	4.1	5	0	0	0	0
2	0.9	36	1.5	4.9	3.2	17	114	38	38	38
3	1.5	20	1.7	5.1	3.0	21	130	6	35	35
4	2.1	13	1.9	5.3	3.6	17	137	8	27	27
5	2.7	11	2.1	5.5	3.9	16	139	9	23	23
7	3.3	9	...	...	...	...	141	20	20	20

Expected acidity after 1.5 grains per gallon of alum was based on the slight amount set free from the neutral sodium carbonate.

REACTION OF CHARLESTON WATER (ALKALINITY 15 P. P. M.) WITH BASIC ALUMINUM SULFATE

Alum. sulf. per gal.	Color	P. p. m.	<i>N</i> /50 Na <sub>2</sub> CO <sub>3</sub> per 100 cc.	Theoretical increase in acidity	Theoretical total free acidity	Actual found	Expected acidity lost expressed as CaCO <sub>3</sub>	Reduction in color	Color equivalent to one acid	Color removed by 1 gr per gal alum
			Cc.	Cc.	Cc.	Cc.				
0	80	0.0	1.2	1.2	0	0	0	0	0	0
1	80	0.8	2.0	2.0	0	0	0	0	0	0
1.5	65	1.2	2.4	2.1	1	10	10	10	10	10
2	27	1.6	2.8	1.8	10	53	5	26	26	26
2.25	14	1.8	3.0	...	...	66	...	29	29	29
2.5	8	2.0	3.2	...	...	72	...	29	29	29
3	8	2.9	4.1	...	...	72	...	29	29	29

(a) Acid to lacmoid showing excess alum.

The expected acidity removed in the last two tables was due to coloring matter alone as there was no complication of excess alum.

#### SUMMARY

From the results of analyses a careful study has been made of the reactions occurring between basic aluminum sulfate and the alkalinity of natural waters on the one hand and between the alum and the color on the other.

The average basic aluminum sulfate from analysis may be represented by the formula  $2\text{Al}_2(\text{SO}_4)_3 \cdot \text{Al}_2(\text{SO}_4)_2(\text{OH})_2$ , a mixture of two parts neutral sulfate and one part monobasic sulfate.

The maximum alkalinity that can react with 1 grain per gallon of this average alum is 8.3 p. p. m. Practice for waters of low alkalinity show only about 6 p. p. m. reacting. High alkalinity waters approach the upper figure.

The amount of carbonic acid set free by one grain per gallon of alum is usually about 3.5 p. p. m.

Based upon this amount of acid produced and six alkalinity used up the equation is written to show the precipitation at ordinary temperatures of  $2\text{Al}_2(\text{CO}_3)_2$ .



(OH)<sub>2</sub>.Al<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>3</sub>, a mixture of two parts monobasic carbonate and one part monobasic sulfate. When represented graphically these reactions seem explainable by uneven stress.

It is maintained that a large part at least of the color is of acid character. The color combines with the hydroxyl radicle of the aluminum precipitate and is removed from solution merely because of the insolubility of the aluminum carbonate, or hydrate. At 100° F. a dibasic carbonate is probably formed and twice as much color is removed for the same amount of alum. At boiling temperature the aluminum probably is completely combined with the color forming a compound that is soluble as are iron compounds. At boiling temperature no precipitation takes place but the color is intensified. This is in line with the fact that with highly colored waters precipitation and color removal does not begin with small amounts of alum, the excess color exerting a solvent effect. These compounds are represented in simple form, neglecting complex sulfates, as Al(CO<sub>3</sub>)R insoluble, Al<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub> insoluble, and AlR<sub>3</sub> soluble.

The direct reaction of alum upon color when added to water in excess of the alkalinity is explained by action upon the neutral color to acidify it, hydrolysis by water then precipitating two-thirds of the color as a monobasic aluminum compound, AlR<sub>2</sub>(OH). The color in this reaction in reality acts like the alkalinity. A high residual color when water is treated with excess alum, the greenish tint produced and the lightening of the color as by an acid confirm this theory. The application of this reaction of excess coagulant at Springfield, Mass., has resulted in color removal twice that produced by the ordinary reaction for the same amount of alum.

The larger amount of alum necessary to use with highly alkaline water, especially sodium carbonate, is probably due to formation of soluble alkaline aluminates.

Experiments with highly colored waters have shown a removal of expected acidity exactly in proportion to the removal of color. This indicates that the color is of acid nature.

The amount of color removed per grain of alum per gallon in different waters was found to be proportional to the color acidity.

Aeration of these highly colored waters left a residual acidity which agreed with the color acidity. Boiling failed to remove the acidity.

Alkalies deepen the natural color of waters, while acids lighten them.

Neutralization of the color acidity by soda prevented decolorization with as small amounts of alum as before neutralization.

Residual colors which cannot be removed by large amounts of alum are frequently explained by combination with iron, the iron preventing the alum from combining.

The fact that definite amounts of alum remove definite and proportional amounts of color points to a definite chemical reaction rather than a physical inclusion.

The recent successful removal of color at Grand Rapids, Mich., by excess magnesium hydrate also points conclusively to the acid character of color.

LABORATORY DIVISION  
DEPARTMENT WATER SUPPLY, GAS AND ELECTRICITY  
NEW YORK CITY

# SOME FURTHER RESULTS OF THE HYPOCHLORITE DISINFECTION OF THE BALTIMORE CITY WATER SUPPLIES—A COMPARISON OF THE REDUC- TION OF THE DIFFERENT MEMBERS OF THE B. COLI GROUP<sup>1</sup>

By J. BOSLEY THOMAS AND EDGAR A. SANDMAN

We have shown in a previous paper<sup>2</sup> some of the results obtained in the hypochlorite disinfection of the Baltimore City Water supplies during 1912, when the disinfectant was applied at the effluent of the impounding reservoir. During 1913 the treatment was continued, pending the completion of a filtration plant, but the chemical was applied at the effluent of the first storage reservoir, after the water had been subjected to a longer period of sedimentation, and had received, during periods of high turbidity, a preliminary treatment with aluminum sulfate. After receiving the hypochlorite treatment the water passes through about a mile of conduit to a second storage reservoir where it is retained for a period of from five to seven days before entering the distribution system.

In addition to the use of the water from this supply, known as the Gunpowder River, another supply, which was seldom used during the previous year, was brought into service again. The water from this supply, known as the Jones Falls, was treated at the impounding reservoir, from which it flows through about a mile of conduit to the first of two storage reservoirs.

The amounts of available chlorine applied to these supplies varied between 0.65 and 2.00 parts per million parts of water. The averages per month are shown in Tables I, II and III.

As in the work of the previous year, the *B. coli* averages were obtained from daily tests made with portions of water varying by a multiple of ten from 0.001 cc. to 100 cc., sufficient tubes being used in each case to secure at least one negative and one or more positive tests, excepting when no fermentation was obtained with 100 cc. Lactose bile was used as an initial medium and Endo's agar for isolating the *B. coli*-like organisms in pure culture. In our previous work no differentiation was made in the members of this group, but later these organisms were divided into four sub-groups by the use of dulcine in addition to the commonly used sugars and gelatin. For the purpose of this classification those organisms causing gas production in lactose, dulcine, saccharose and dextrose without liquefaction of gelatin were considered to be *B. coli communior*; those causing gas production in lactose, dulcine and dextrose without liquefaction of gelatin were classified as *B. coli communis*; those

<sup>1</sup> Read before the Section of Water, Sewage and Sanitation at the 49th Meeting of the American Chemical Society, Cincinnati, April 6-10, 1914.

<sup>2</sup> THIS JOURNAL, 5, 476.

TABLE I—MONTHLY AVERAGES OF BACTERIAL COUNTS OF THE BALTIMORE CITY WATER SUPPLIES BEFORE AND AFTER TREATMENT—GUNPOWDER RIVER SUPPLY

	FIRST STORAGE RESERVOIR				EFFLUENT				SECOND STORAGE RESERVOIR				EFFLUENT			
	Influent		Bacteria per cc. growing at		P. p. m. Tur- available chlo- ride-bid- ity		Bacteria per cc. growing at		Bacteria per cc. growing at		Tur- bid- ity		Bacteria per cc. growing at		Tur- bid- ity	
	G. per gal. coagulant added	Tur- bid- ity	37° C.	20° C.			37° C.	20° C.	37° C.	20° C.			37° C.	20° C.		
January	11	270	2,800	0.65	9	75	27,000(a)		8	32	14,000(a)		8	32	14,000(a)	
February	9	55	5,500	0.80	7	24	750		6	12	14		6	12	14	
March	8	36	1,900	0.85	6	32	1,200		5	9	39,000		5	9	39,000	
April	0.692	49	1,100	0.80	8	110	4,800		9	16	11,000		9	16	11,000	
May	0.532	38	600	0.80	7	140	1,800		13	15	7	27	7	27	2,100	
June	0.803	44	170	0.85	6	160	450		14	95	10	10	10	10	85	
July	0.931	85	380	1.00	8	47	180		20	42	11	10	12	12	3	
August	1.237	80	470	1.50	8	55	90		11	14	9	5	3	3		
September	1.207	95	880	1.75	8	90	140		1	1.5	8	1	2	2		
October	1.144	80	750	2.00	7	60	110		0.6	0.3	6	0.4	0.3	0.3		
November	0.633	45	2,200	1.75	7	160	2,100		0.8	1	6	3	0.9	0.9		
December	0.604	19	200	1.50	6	42	28,000		4	5	5	0.9	1.1	1.1		

(a) After-growths resulting from treatment formerly conducted at the impounding reservoir.

causing gas production in the three sugars but not in dulcite with or without liquefaction of gelatin as *B. lactis aerogenes*; and those causing gas production in lactose and dextrose only were called *B. acidi lactici*. It should be borne in mind that this is but a general classification, and it cannot be claimed that the or-

many of the liquefactions occurred after the first two weeks and that some showed only slight signs of liquefaction at the end of a month. And, again, it is an open question whether the *B. acidi lactici* is a true type or, after all, only a form of *B. coli communis*. It is not within the province of this paper to consider

TABLE II—MONTHLY AVERAGES OF BACTERIAL COUNTS OF THE BALTIMORE CITY WATER SUPPLIES BEFORE AND AFTER TREATMENT—JONES FALLS SUPPLY

	IMPONDING RESERVOIR				SUPPLY FIRST STORAGE RESERVOIR								SECOND STORAGE RESERVOIR			
	EFFLUENT		Bacteria per cc. growing at		G. per gal. coagulant added	EFFLUENT		Bacteria per cc. growing at		Turbidity	EFFLUENT		Bacteria per cc. growing at			
	P. p. m. available chlorine	Turbidity	37° C.	20° C.		37° C.	20° C.	37° C.	20° C.		37° C.	20° C.				
January	1.50	23	390	10,000	0.617	100	2,800	19	95	6,500	22	100	3,800			
February	1.50	11	75	490	0.664	36	36	6	22	12	7	27	15			
March	1.50	22	150	2,100	0.585	90	480	21	45	130	21	43	190			
April	1.50	40	430	5,000	0.938	240	1,800	60	250	750	34	130	420			
May	1.50	30	160	650	0.581	95	150	17	70	140	8	29	55			
June	1.35	13	110	470	0.000	65	250	16	140	2,000	7	45	500			
July	1.50	17	220	950	0.000	110	1,300	11	170	1,000	7	23	370			
August	1.75	22	800	1,100	0.753	80	160	8	180	460	7	28	130			
September	2.00	35	850	4,100	0.719	95	95	15	12,000	25,000	7	95	220			
October	2.00	29	600	4,200	0.694	55	20	600	2	5,500	6	38	100			
November	1.75	12	210	1,800	0.430	50	450	9	50	15,000	4	13	600			
December	2.00	15	140	18,000	0.000	35	800	10	43	430,000	6	13	20,000			

ganisms in all cases were strains identical with the classical types. Some of the cultures classified as *B. lactis aerogenes* A<sub>3</sub>, in accordance with the last report of the Committee of the American Public Health Association on standard methods of water analysis, no doubt, were species of cloacae capable of causing

this matter further, but we would say that, although some of the strains of so-called *B. acidi lactici* undoubtedly show signs of motility, there seems to be a fundamental difference between them and the classical type of *B. coli communis* in that they cannot be made to cause gas formation in dulcite.

TABLE III—YEARLY AVERAGES OF BACTERIAL COUNTS AND *B. COLI* TESTS OF THE BALTIMORE CITY WATER SUPPLIES BEFORE AND AFTER TREATMENT—GUNPOWDER RIVER SUPPLY

	First storage reservoir		Second storage reservoir		Impounding reservoir effluent		First storage reservoir		Second storage reservoir effluent	
	Infl.	Effl.	Infl.	Effl.	Infl.	Effl.	Infl.	Effl.	Infl.	Effl.
	G. per gal. coag.	Turbidity	G. per gal. avail. Cl.	Turbidity	G. per gal. avail. Cl.	Turbidity	G. per gal. avail. Cl.	Turbidity	G. per gal. avail. Cl.	Turbidity
G. per gal. coag.	0.865	1.19	0.865	1.19	1.65	1.65	0.498	0.498	0.498	0.498
P. p. m. avail. Cl.	47	7	47	7	22	22	18	18	14	14
Turbidity	600	86	600	86	350	350	85	85	49	49
Per cent reduction.	8,000	3,600(u)	8,000	3,600(u)	4,000	700	40,000(c)	2,200	2,200	2,200
Bact. per cc. at 20°	55	55	55	55	83	83	0.016	0.016	0.008	0.008
Per cent reduction.	1.638	0.219	1.638	0.219	0.001	0.001	0.063	0.063	0.08	0.08
<i>B. coli communis</i>	86	86	86	86	99(b)	99(b)	0.009	0.009	0.143	0.143
Per cent reduction.	5.034	0.389	5.034	0.389	0.010	0.010	3.030	3.030	0.96	0.96
<i>B. coli communis</i>	92	92	92	92	98(b)	98(b)	3.177	3.177	0.231	0.231
<i>B. lactis aerogenes</i>	5.363	0.467	5.363	0.467	98(b)	98(b)	1.373	1.373	0.93	0.93
Per cent reduction.	3.181	0.459	3.181	0.459	0.012	0.012	0.112	0.112	0.048	0.048
<i>B. acidi lactici</i>	85	85	85	85	97(b)	97(b)	92	92	97	97
Per cent reduction.	85	85	85	85	97(b)	97(b)	92	92	97	97

(a) Eleven months' average, January being excluded on account of after-growths resulting from treatment formerly conducted at the impounding reservoir.

(b) Based upon first storage reservoir effluent, and therefore showing reduction due to hypochlorite.

(c) After-growths during several months.

(d) After-growths during September.

gas production in lactose, while some others which at first could cause no gas production in lactose were found, after repeated rejuvenation, to produce this change. Furthermore, it is doubtful whether four weeks is long enough time for the observance of liquefaction. We made readings at the end of two weeks and again after four weeks, and found that

The enumeration of bacteria was made upon standard agar at 37° C. and at 20° C. The ratio of the yearly average of those organisms growing at 37° C. to those growing at the lower temperature was about 1 to 10, with a somewhat higher ratio in the winter months. The organisms growing at 20° C. suffered a greater percentage reduction from the effect of the

hypochlorite than those growing at 37° C., which may be due, in part, to the fact that there was a greater number originally present, and because the saprophytic organisms may be more vulnerable to the treatment. These reductions were 99 per cent and 85 per cent, respectively, in the Gunpowder River supply, and 83 per cent and 76 per cent, respectively, in the Jones Falls supply. On the other hand, the preliminary storage and sedimentation with rather constant use of a coagulant effected a reduction of only 55 per cent of the organisms growing at 20° C., whereas the organisms growing at the higher temperature were reduced by 86 per cent. The four sub-classes of the *B. coli* group were all reduced by nearly an equal amount which varied between 97 per cent and 99 per cent. The *B. lactis aerogenes* and *B. acidi lactici* suffered the least reduction, but the difference is so slight that, although based upon some fifteen hundred isolations, the results do not warrant any conclusion that these types are any less vulnerable to the treatment than the true *B. coli communis* or *B. coli communior*.

During the time when the amount of available chlorine applied exceeded 1.50 parts per million there was frequently observed in the water from the city taps an odor of chlorine, or an odor apparently due to chlorine, and the presence of residual chlorine could be demonstrated by chemical tests; but with the use of 1.50 parts or less few complaints were received, although trouble was still encountered by the ice companies using this water for the manufacture of ice. The odor was most noticeable in the core ice where it becomes segregated as the water freezes, and as distillation of the water before freezing does not remove this odor, it would seem that the chlorine is in some organic combination that passes over with the distillate.

The number of cases of typhoid fever occurring in Baltimore during 1913 was seventeen per cent less than an average of the number of cases occurring during the five years from 1906 to 1910 before the treatment was instituted.

WATER DEPARTMENT, BALTIMORE

### A SANITARY SURVEY OF WHITE RIVER<sup>1</sup>

By JOHN C. DIGGS

During the summers of 1908 and 1910 the Water Department of the Indiana State Board of Health made investigations of the sanitary condition of the waters of the southern end of Lake Michigan and of the Calumet River. These surveys disclosed such grossly polluted conditions that it seemed wise to continue similar work on the other streams of the State. In 1911 that portion of the Ohio bordering Indiana was studied and in 1912 attention was given to the Wabash River. These investigations proved both of these streams to be seriously polluted by domestic sewage and manufacturing wastes.

In 1913 the west fork of White River, a stream rising in and traversing its entire course through Indiana, was selected for study. White River is not a large stream, but it is of great importance as a source of water supply for many Indiana cities.

<sup>1</sup> Presented at the 49th Meeting of the American Chemical Society, Cincinnati, April 6-10, 1914.

The watershed of the west fork of this stream has an area of 5,034 square miles (one-seventh of the total area of the State). The population of the drainage basin is approximately 638,000. The rural population is 275,000 and the urban 363,000. The average population for the entire basin is 127 per square mile. The highest density, 664 per square mile, is in Marion County, the seat of Indianapolis.

Although the valley of the river is only 275 miles in length, the course of the stream covers 388 miles, due to meanderings and many short curves. Throughout the upper portion, the river is small and very rapid, but from Indianapolis to its mouth it is sluggish and flows in a wide channel.

In the study of the conditions of the stream, attention was given to the following features:

#### 1.—General features of drainage basin.

- a Topography and geology
- b—Principal tributaries.
- c—Gradient.
- d—River stages and river flow.
- e—Precipitation.
- f—Population of watershed.

#### 2.—Water works system.

#### 3.—Sewage systems and sewage disposal.

#### 4.—Disposal of garbage and night soil.

#### 5.—Manufacturing wastes.

#### 6.—Oil well wastes.

#### 7.—Typhoid fever.

#### 8.—General sanitary condition of cities.

#### 9.—Sanitary condition of White River.

#### 10.—Chemical and bacterial analyses.

a—From White River, including study of cross river and depth of samples.

b—Samples from tributaries.

c—Samples from cities and towns.

(1) Public: (a) surface supplies; (b) ground waters.

(2) Private: (a) wells; (b) springs; (c) cisterns.

The upper portion of the stream was surveyed on foot and by means of a row boat. Samples were collected at frequent intervals from the river and sent to the laboratories of the State Board of Health at Indianapolis for analysis. From Martinsville, a point 43 miles below Indianapolis, to the mouth of the river the work was conducted from a floating laboratory. This was a house boat 40 feet long by 13 feet wide, stern wheel paddle, equipped with room for laboratory, living and sleeping quarters. The surveying party consisted of four to five men made up partially of students taking scientific courses in the State Universities.

Samples were collected at points in the river as the boat moved down stream. Stops of several days were made at towns bordering on the river. At these places samples were collected from public and private water supplies and sanitary surveys of the towns conducted. During the course of the work a total of 779 samples of water were collected and analyzed (391 river samples and 388 from private water supplies, driven wells, dug wells, cisterns and springs); 45 per cent of this number were good, 40 per cent bad and 15 per cent of doubtful quality.

Of the 197 dug wells which were examined, only 50



or 25 per cent were good, 58 per cent were bad and 16 per cent classed as doubtful; 11, or 72 per cent, of the 154 driven wells examined, were found to be good, 12 per cent were bad and 16 per cent of doubtful quality. Of 7 springs examined, 3 were good, 3 bad, and 1 doubtful.

At the time of the collection of the samples special notice was given to the sanitary condition of the backyard in which the well or cistern was located. In some places as many as half a dozen wells and a dozen privies (the unsanitary type) occurred within a radius of 100 ft. In most cases the soil was made up largely of gravel, allowing at least a fair filtering material. In one instance, Gosport, Indiana, the wells occurred in a stratum, locally known as Mitchell limestone. This is a very extensively fissured material and quite soluble. Practically all the wells of the town draw their supply from the same vein, or underground stream of water. When one owner cleans out his well, the neighboring wells are muddied. From the analyses of these supplies it was quite evident that this same underground stream served the double duty of water supply and sewerage system.

In carrying on the investigations in towns, coöperation of local health officers was obtained. Many of the unsanitary conditions were remedied and polluted wells abandoned.

This paper can hope to give no more than a mere outline of the work done. Detail of the methods employed will be found in the 1913 report of the Indiana State Board of Health.

From the inspection of local conditions, study of water supply (public and private) and methods of sewage disposal much information has been obtained which will be of great value to the public of the State.

White River is a comparatively small stream, yet it is used as a source of public water supply and sewage disposal for over 300,000 people. It is seriously polluted and in many places a great detriment not only to the health of persons using it as a supply, but in some places to persons living along its banks.

Many private supplies of the State are seriously polluted. This especially applies to dug wells.

This survey shows need of legislative power to be vested in central authority, naturally the State Board of Health, whereby the rivers, our natural resources, can be saved for the future generations. The public is beginning to realize that it is not properly conserving its resources when it permits the streams of its State to be defiled by the refuse of its cities. But public opinion is slow to form and the need of education is decidedly apparent. To collect data regarding the unsanitary conditions of the streams, to determine the tremendous amount of waste which goes into them and to point out to the public the number of deaths and amount of sickness which may be traced back to the polluted water, become the duties of health departments. But education, in many cases, will not cause the packer to cease dumping his offal into the streams. Then it becomes the duty of the health authorities to present to the legislative bodies facts concerning the unsanitary conditions and their causes,

that the health of the public may be sought before the financial gain of an individual.

INDIANA STATE BOARD OF HEALTH  
INDIANAPOLIS

## AN INVESTIGATION INTO THE CHEMISTRY OF LAUNDERING<sup>1</sup>

By W. F. FARABIER  
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The laundry industry is one of a group which are not usually classified as strictly chemical industries, but which, nevertheless, depend in large measure upon the proper control of chemical reactions for their successful operation. The list includes, among others, bakeries, glass factories, brick plants, brass and iron foundries, confectioneries, tanneries and creameries. Although the laundry industry is one of the most important, both in point of the nature of the service it renders modern civilized communities and of the number of employees and the capital invested,<sup>2</sup> it is perhaps the last to avail itself of the benefits to be derived from an extensive adoption of the methods and teachings of chemical and engineering science.

A great deal of ingenuity has been displayed in bringing the processes and machinery employed to their present state, but investigation shows that before the industry may rightfully be classed as an efficient one, much improvement is necessary, especially in the case of the chemical processes which occur either as essential parts of the operation, or as harmful accompanying reactions.

As a result of the study given to the production of high-grade laundry work by the more progressive men engaged in the industry, empirical methods are now quite generally employed in the best plants which leave little to be desired as far as the appearance of the finished articles is concerned. But for the purpose of investigating the possibility of introducing more scientific methods, which would improve conditions by prolonging the period of usefulness of the articles laundered and also by reducing the cost of production of the work, the experiments to be described were carried out.

The work of the laundry is necessarily complex, but may be conveniently divided into a number of parts. Exclusive of the collection and delivery of the bundles, and of the marking and listing of the articles in each bundle to make possible their return to the respective owners, the following operations may be enumerated: sorting, washing, extracting, that is, the removal of excess water by means of centrifugal machines, starching, drying, dampening, ironing, and finally finishing or folding into neat compact form, and sorting into lots to be tied up later into bundles.

<sup>1</sup> These data represent a part of the work done during the author's tenure of the Alden Speare Fellowship (September, 1907, to December, 1909). The work was carried out under the direction of the late Dr. Robert Kennedy Duncan, to whom the author owes much for valuable advice and encouragement. The author wishes also to express his appreciation for the helpful assistance rendered by Dr. Hamilton P. Cady.

<sup>2</sup> The census of 1910 included power-laundries for the first time. The number of plants reported is 5184. This does not include the laundries in hospitals, public institutions and shirt and collar factories. A careful study of conditions in Chicago indicates an annual volume of business close to \$3,000,000.

Obviously, many of these operations have little to do with chemical processes, and it is only with the washing that these experiments are concerned. In fact, it is this part of the process alone which is distinctively chemical, and which seems most largely responsible for the complaints now made against the results obtained in well managed laundries.

On account of the great variety of articles brought to the washroom, it is evident that different treatment must be accorded to the different kinds of fabrics. The only classes which are of great importance are those consisting of articles made from cotton, linen, silk and wool. Greater diversity is caused, however, by the very large list of dyestuffs which are now employed on all of the above groups.

In the case of undyed fabrics of cotton or linen, the treatment employed is, perhaps, the most drastic, and it is largely on account of the too early disintegration of articles of this class that complaints are justly and so frequently made. Since all articles are submitted to the less harmful operations employed in the case of these undyed articles, the experiments were carried out in accordance with the modern practice of handling such articles as are made from cotton and linen only, and which have not been dyed. This seems justifiable, because these articles form the largest part of the work done, and also because the effects produced are necessarily similar in so far as the various operations are duplicated in the case of the other classes of articles. This does not apply to the effect on the dyestuffs, but rather to the weakening of the fabrics. The former problem was not taken into consideration here.

In the sorting room, all articles are separated into lots, according to the kind of fabrics, the nature of the dyestuffs, and finally the extent to which the articles are soiled. Since these different lots are to be washed differently, this separation is preserved throughout the whole course of treatment.

#### WASHING MACHINES USED IN LAUNDRIES

The machines in which the washing is done consist of two concentric cylinders separated by a space of several inches. The outer cylinder is stationary and is carried on a metal stand for securing the whole machine in position. It is provided with the necessary boxing and gearing for causing the inner cylinder to revolve and to reverse automatically after several revolutions in one direction. It has also pipes for introducing hot and cold water and live steam, and a drain pipe for discharging the liquids after they have done their work. The inner cylinder into which the articles are placed, is perforated so that the liquids may have free access to the fabrics. Both cylinders are provided with suitably hinged doors, so that the articles may be readily introduced and removed. The sizes of the machines vary from small ones, washing fifty shirts, to very large ones, which can handle five hundred shirts at one time. After the articles are placed in the machine they are not removed until they have been cleansed and given the proper color by means of detergents, bleaches and bluing materials. The different solutions are introduced in order and

run off after they have performed their respective functions.

The principle upon which the washing is effected is simple. By the revolution of the inner cylinder, the articles are carried part way up the sides, and then fall down into the solutions, causing the latter to be forced through the fabrics, and thus insuring intimate contact between the detergents and the substances to be removed.

#### LAUNDRY PROCESS IN GENERAL USE

In order to proceed with the problem in hand, the first step was the investigation of the process in general use, in order to determine what parts were defective, and the causes for, as well as the nature of the harmful results produced.

The machine of average size will permit the washing of about one hundred shirts, weighing about seventy-five pounds. The volume of the different solutions used in such a machine is approximately twenty-five gallons. The method of washing is as follows: Cold or luke warm water is admitted and the machine is allowed to run for from five to ten minutes. Very frequently sufficient sodium carbonate, or so-called neutral washing soda,<sup>1</sup> is added to make from  $\frac{1}{4}$  to 1 per cent solution. The water, or weak alkaline solution, removes some of the starch from starched goods, carries off surface dirt and dissolves stains of an albuminous character, which otherwise might be set by coagulation of the albuminous substances, if hot water were used at once.

Warm water is next admitted and soap added together with some alkaline substance, such as sodium carbonate, neutral washing soda, caustic soda or borax. The first two are the ones most frequently used. The soap is used in from  $\frac{1}{4}$  to 1  $\frac{1}{4}$  per cent solution, and the alkaline substance in about the same strength. Steam is then admitted and the temperature brought to the boiling point in from ten to twenty minutes. The time of running in this solution is usually from twenty to thirty minutes.

This solution is discharged and another of from  $\frac{1}{2}$  to  $\frac{2}{3}$  the strength of the first is added. In some instances a hot rinse is given between the two solutions

<sup>1</sup> These sodas are mixtures of sodium bicarbonate and sodium carbonate. Analyses which are perhaps typical for articles of this kind are:

Na <sub>2</sub> CO <sub>3</sub> .....	46.3	36.1
NaHCO <sub>3</sub> .....	37.7	50.0
H <sub>2</sub> O and impurities.....	16.0	13.9
	100.0	100.0

These articles find large sale because they do not yield as strongly alkaline solutions as when sodium carbonate alone is used. The hydrolysis of the sodium carbonate is less extensive in the presence of the bicarbonate than when alone. Theoretically, it is possible to prepare a solution from sodium carbonate which will have the same concentration of hydroxyl ions as is present when a given concentration of these neutral sodas (so-called) is employed. The weight of sodium carbonate is in every case less than that of the neutral soda, and as the price of the two products is nearly the same, a material saving can thus be effected. The difficulty met with in the laundries seems to be attributable to the fact that in replacing a neutral soda by sodium carbonate, the same weight is used, owing to ignorance of the above conditions, and this naturally yields a solution which is too strongly alkaline. Several plants have been induced to decrease the quantity of sodium carbonate to half (or even less) of that used in the case of the neutral sodas, and results have been obtained which are satisfactory in every respect. Summer soda crystals have also been used as a neutral soda (Na<sub>2</sub>CO<sub>3</sub>·NaHCO<sub>3</sub>·2H<sub>2</sub>O).

in order to carry off the remaining dirty suds. The bleach is also added in this second suds, and the whole run for about the same length of time as the previous one. The bleach used is prepared by adding sufficient sodium carbonate to bleaching powder to convert the calcium salts into the more soluble sodium salts. This has the advantage that none of the soap is decomposed with the formation of lime soap, as would be the case if bleaching powder itself were used. The quantity of bleach used varies from the equivalent of  $1/4$  to  $3/4$  of a pound of commercial bleaching powder. The bleach liquor is generally added at the beginning of the run, the steam being admitted so as to bring the temperature to the boiling point in from fifteen to twenty minutes. The boiling is continued, and the whole time of run made from twenty to thirty minutes. From two to four hot rinses follow this suds-bleach treatment.

The next solution is an acid bath. The acids most frequently used are acetic and oxalic. Sufficient acid is added to make the solution about  $N/50$  (equivalent). This acid is used for the purpose of neutralizing any alkaline substances which have not been rinsed out, and to cause the aniline blue, which is used subsequently, to produce an even color. If the blue is not added in the acid bath, it is used in the next water. From one to four rinses, sometimes hot, sometimes cold, are given after the bluing.

After the above course of treatment the articles are removed from the machine and placed in the basket of a centrifugal machine, in order to remove the excess of water. Articles which need no starching are usually ironed at once after removing from the centrifugal machine, while the others are sent to the starch room. After starching, all articles are dried by being placed in a drying-room heated to  $100^{\circ}$  C. by steam coils, and provided with a ventilating fan for removing the moist air. After dampening to the proper degree, the ironing and shaping are next done.

#### PRELIMINARY EXPERIMENTS ON DIFFERENT PARTS OF ABOVE PROCESS

The first plan adopted for comparing the harmful effects of the different parts of the process outlined above, was to take four series of turnover collars, five to a series, and submit each series to one of the above parts of the washing process, that is, one series to the soap-alkali, one to the bleach, one to the acid and one to water only, in order to have a check on the mechanical effects produced in the washer and in the ironing machines. After each treatment in the laboratory wash machine, under conditions as nearly as possible like those obtaining as an average in general practice, the collars were rinsed (except in the case of the acid series), then taken to a custom laundry to be starched and ironed. The plan was to repeat this treatment in each case until the edges of the collars broke, thus showing the relative harmfulness of the different treatments.

The quantities of soap and soda ash used were 190 grams soap and 95 grams of soda ash per gallon of solution. These quantities are larger than those generally employed, but were chosen rather than quanti-

ties below the average. The soap used was a neutral soap made from good red oil or commercial oleic acid, and analyzed as follows:

Water	20.7
NaCl as soap	9.3
Fatty acid anhydrides	69.3
Soda ash	0.1
NaCl	0.2
Unaponified	0.1

The soda ash was analyzed and found to be a good commercial product, containing only a small percentage of soluble and insoluble impurities.

The bleach solution was made by taking 12.5 grams of bleaching powder and 8.2 grams of soda ash per gallon of water. It was necessary to add sufficient cloth so that the ratio of the weight of cellulose to the weight of the solution might be comparable to that in practice. The bleaching powder was analyzed and found to contain 26.8 per cent available chlorine. It was a sample obtained from a custom laundry and was of poor grade. The acid used was oxalic and a sufficient amount of it was added to make the solution approximately  $N/50$ . As has been stated above, no rinse was given after the acid was used, although most laundries now rinse at least once. However, at that time many plants were found which did not rinse subsequently, and this more severe test was made in order to compare its effects with the bleaching which was expected to prove quite harmful. The results obtained were as follows:

*Bleach Series:* Two broke on 7th time; one on 8th; all on 9th time.  
*Acid Series:* One broke on 5th time; one on 6th; two on 7th; all on 9th time.  
*Soap and Alkali:* All intact 15th time.  
*Water:* All intact 15th time.

The last two series were lost on account of an accident in the laboratory, but they had run sufficiently long to establish the fact that under the conditions of the tests the acid and the bleach are the most destructive chemicals employed. Other series which were comparable to the soap-alkali series were later run as high as twenty-five times before a break occurred, showing that the conclusions drawn above were justified.

#### THREAD ADOPTED FOR TEST PIECES

The above method was not considered satisfactory for further comparisons, because of the length of time necessary to carry it out and also because of the uncertainty of being able to give all of the collars the same treatment during the starching, ironing and finishing. For this reason the method of determining the breaking strengths of test pieces before and after the various treatments was adopted. On account of the difficulty encountered in attempting to use test pieces in the form of strips of cloth or skeins of yarn, for the reason that it is almost impossible to distribute the strain equally throughout the pieces, the use of single threads as test pieces was decided upon. It was thought that the warp or weft threads of a good grade of muslin or linen cloth might be used, but these were found to be too irregular to make their use advisable. The most suitable material that could be found was a good grade of white thread.

#### TESTING MACHINE USED

The testing machine used was designed and made in the University Instrument Shop. It is similar in



principle to the machines which are in general use for determining the tensile strength of paper. The test piece, about five inches in length, is fastened between two clamps, and the force is applied by causing a weighted arm, to which one end is clamped, to move through an arc by turning a geared wheel which moves a slow-motion screw to which the other clamp is fastened. A scale graduated by means of known weights is placed in front of the weighted arm, and the position of the arm at the time of breaking is marked by a light rider which is caused to move along the scale.

#### METHOD OF TESTING

Because of the fact that thread is not uniform in cross-section and in the twist, that is, the number of turns per inch due to the spinning, the breaking strengths of pieces from the same spool show large variations. Numerous tests showed that the strength for a No. 20 thread ranged from 1300 to 1900 grams. On account of this great variation it is necessary to employ a large number of test pieces in each series, in order that the mean value may be significant. The thread was sampled by taking every twentieth length of five inches for twenty series of one hundred test pieces each.

Experiments made with a number of these series, after the sizing materials had been removed by boiling the threads for an hour in 1 per cent sodium carbonate solution, showed that the different mean values agreed satisfactorily, usually well within one per cent. With this agreement, the method seems well adapted for making comparisons of the effects of different chemicals, used under various conditions, upon the tensile strengths of cotton thread. It is evident that the breaking strength is closely related to the wearing qualities of threads, and hence of pieces of fabric, under the conditions to which they are subjected in use.

It was found that different spools of thread differed from one another more than the series of threads from one spool differed from each other. For this reason it is necessary to determine the breaking strength for each lot of threads prepared.

#### COMPARISON OF METHOD WITH PRELIMINARY EXPERIMENTS

Tests were run upon threads, employing solutions of the same kinds and of the same strengths as were used in the experiments on the collars. After each of the processes had been repeated ten times the breaking strengths were determined. The conditions were made as nearly the same as possible, both as regards the times of treatment and ratios of the weights of solutions to the weights of cellulose. The results were as follows:

Original breaking strength, ave.....	1724 g. (1722, 1723, 1724, 1726)
Soap-alkali series.....	1861 g.
Bleach series.....	181 g.
Oxalic acid series.....	265 g.

The probable error in the original figured by method of least squares is  $\pm 7$  grams. These figures confirm the results of the practical tests with collars, and the agreement speaks in favor of the use of the new method which is more rapidly carried out and is more easily controlled.

As has been stated above these results do not permit the drawing of conclusions concerning the actual amount of damage done in the different processes in the best plants. The figures do, however, indicate the parts wherein most care must be exercised and in which improvements are most needed.

The soap-alkali treatment is, perhaps, the least harmful of all the different operations. Experiments showed, however, that if the quantities of alkaline substances were not kept low, the threads were attacked and, although the breaking strength was not affected as greatly as in the bleach and acid series, the appearance suffered, owing to the formation of a woolly coating of loose ends of fibers. The damage done in the acid bath is easily made less than in the case of the tests, for thorough rinsing will remove the acid and prevent its doing damage in the dry room or in the ironing machines.

#### REACTIONS OF CELLULOSE

Cellulose, which is chemically one of the most inactive of the carbohydrates, is nevertheless extensively attacked by acids, alkalies and bleaches under conditions which often exist in laundries. In the presence of hydrogen ions, cellulose is converted into another substance, hydrocellulose, which differs from the former in many ways. The most important difference for the purpose in hand is that hydrocellulose is a friable substance and, therefore, is valueless under the conditions to which fabrics are subjected in use.

The acid solutions employed in laundry work are relatively dilute, and the extent to which the cellulose is acted upon while in these solutions is small. It is essential, however, that the acid be thoroughly removed because when the articles are placed in the drying room, or are caused to pass over the heated surfaces in the ironing machines, the dilute acid is concentrated and this, together with the high temperature, produces rapid conversion of the cellulose. This practice of rinsing after the acid is discharged is now quite general and is a decided advance in the right direction.

The velocity of this reaction is proportional to the concentration of hydrogen as ion present, and is also greatly accelerated by rise in temperature, in accordance with the general rule for the effect of temperature on chemical reactions.

#### REAGENTS USED IN TESTS

As has been stated, the soap and soda ash used were of good quality. Very different results have been obtained by others when the soaps and sodas used were adulterated. Dr. Kind<sup>1</sup> has carried out a large number of experiments and has proved conclusively that detergents which contain large percentages of silicate of sodium cause a rapid deterioration in cotton and linen fabrics. Kind attributes this effect to the action of the hydroxyl ions formed by the hydrolysis of the silicate and to the deposition in the fibers of silicic acid, and also of insoluble silicates which are formed when hard water is used. These deposits are shown to be very extensive under some conditions,

<sup>1</sup> "Die Wirkung der Waschmittel auf Baumwolle und Leinen." A. Ziemsens Verlag, Wittenberg, 1909.

amounting, in one case where a series of test threads were washed thirty times in a 2 per cent solution of 38° Bé. sodium water glass, to 14.2 per cent. The water glass analyzed 27 per cent silicic acid and 0.12 per cent free caustic soda. These threads were brittle owing to the presence of the encrusting substances which did not allow the fibers to yield when subjected to a bending strain, and the threads were also weak on account of the disintegration caused by the loosening up and separation of the fibers composing the thread. Kind's work shows that the action is more severe in the case of linen than of cotton.

In the case of soaps and sodas which contain peroxides and perborates, Leimdoerfer<sup>1</sup> has shown that the harmful effect is also great.

The presence of rosin in soaps has been shown to be objectionable because of the fact that the rosin acids which are formed by hydrolysis of the soap settle in the fibers and produce a decided yellow cast in the finished products. Professor Herbert Jackson<sup>2</sup> has shown that soaps which contain as little as 5 per cent rosin are objectionable for this reason.

Many sodas have been found to contain adulterants: some harmful, as sodium silicate and caustic soda, and some inactive, such as common salt and sodium sulfate. It seems certain from the above tests, however, that if pure soap and pure alkalies are used in quantities no larger than are necessary, the weakening of the fibers treated is not very great.

#### ACTION OF ALKALI

The following experiments were performed, using solutions of sodium carbonate which are much stronger than those used in practice. The threads were suspended from cords in the boiling solutions and were provided with glass weights to keep them immersed. The boiling was done in open beakers and the water removed by evaporation was replaced at regular short intervals. The times of boiling, strength of solutions and position of the test threads were as indicated.

The reason for exposing some of the series to the action of both the alkaline solutions and the air, was to determine whether or not the weakening produced was greater under these conditions than when oxygen was excluded by complete immersion. Text books describing the manufacture of textile fabrics generally state that cellulose must not be exposed to the air when it is being boiled in alkaline solutions because the oxidation of cellulose which occurs under these conditions will render the fabrics tender.

Original breaking strength, ave	1696 (1693, 1709, 1696, 1684)
Boiled in 1 per cent $\text{Na}_2\text{CO}_3$ 5 hrs., one half exposed to air and one-half immersed in the solution	1711 1666
Same as above, but completely immersed	1634, 1634
Boiled in 2.5 $\text{Na}_2\text{CO}_3$ for 3.5 hrs. half immersed	1648
Same as one above but completely immersed	1636
Boiled in 5 per cent $\text{Na}_2\text{CO}_3$ for 3.5 hrs., immersed completely	1625, 1622
Same as above, except half immersed	1627, 1610

These results show that even if much stronger solutions than those ordinarily used are employed, the

<sup>1</sup> "Wash, Bleich, Blan, Staerke und Glanz mittel." L. Andes, 1909, Hartleben, Wien, p. 14.

<sup>2</sup> Cantor Lectures for 1907, p. 12.

damage done is not excessive. The color, however, is not so clear, and the same roughening of the threads mentioned above is noticed. The formation of lint is also greatly increased when large quantities of alkali are used.

Since the boiling of threads, even in quite strongly alkaline solutions, does not produce great deterioration, it was thought well to determine the effect of alkalies which are not completely rinsed out. The tests were made by dipping the test pieces into a 1 per cent sodium carbonate solution, squeezing dry by hand to about the same extent as would be the case in a centrifugal machine, and then placing in a drying oven heated to 100°. This process was repeated ten times, rinsing with distilled water between each treatment, and the breaking strength determined. Repeated weighing of the dry threads and also of those which had been wrung after dipping into the solutions showed that a weight of the solution about equal to that of the threads was retained. It was possible to get the amount of solution retained to agree to within about two per cent. The result was as follows:

Original strength	1696
After ten treatments	1420

It is, therefore, very necessary that the alkali be removed by rinsing and by the acid bath which is given later, as otherwise both the color of fabrics and their wearing qualities suffer markedly.

#### RINSING

**HOT WATER**—The advantage of using hot water for rinsing is obvious, for if cold water is used and soap is present in the hot fabrics in quantities larger than are soluble in the cold water, this soap will be precipitated and will redissolve slowly. All of the substances which are to be removed are more soluble in hot water than in cold, and in addition diffuse more rapidly with rising temperature. Consequently hot water is the more desirable.

**HARD WATER**—Since hard water forms difficultly soluble calcium and magnesium soaps with the soluble sodium soap remaining after the washing process and as these do not form a suds, rinsing appears to be more quickly and efficiently done with hard water than with soft. In order to test this assumption which is general among launderers, the following experiments were made:

Pieces of cloth of about the same size were weighed under the same atmospheric conditions, when air-dry. These pieces were then dipped into and washed about in the soap solution such as has been used throughout this work. Some of the pieces were then rinsed three times in tap water and some in distilled water, care being taken to give the test pieces the same mechanical treatment. The tap water analyzed 14.5 degrees of hardness. After standing until air-dry the pieces were reweighed under the same atmospheric conditions. The results were as follows:

Weight in grams	No. 1	No. 2
Of cloth after rinsing in soft water	22.074	21.510
Of cloth air-dry at start	21.877	21.396
Of substances retained	0.197	0.114
Of cloth after rinsing in hard water	22.230	21.643
Of cloth air-dry at start	21.895	21.394
Of substances retained	0.335	0.249

**DISTILLED WATER**—The last rinse water in the case of the pieces rinsed in distilled water was soapy and considerable suds was formed. However, the weighings show that the rinsing was much more efficient in the case of the distilled water series. This is due to the fact that the insoluble soaps which are formed in the fibers when hard water is used are very difficult to remove.

Upon drying the different pieces in an oven at 100° for thirty minutes, the pieces rinsed in soft water were of much better color than the others. Pieces which were allowed to dry at room temperature showed after several weeks a much yellower color in those rinsed with hard water than in those rinsed with soft water.

That rinsing with soft water is advantageous is shown by the observation that the color of articles laundered in plants where this is the custom is uniformly better than that obtained in other plants.

#### DEPOSITION OF SALTS IN FIBERS OF FABRICS

A reason for the breaking of threads in fabrics which is thought by launders to be, perhaps, the most frequent is the deposition in the fibers of calcium carbonate and lime soaps or the crystallization of soluble salts such as sodium chloride or sodium sulfate.

A saturated solution of slaked lime was neutralized with acetic acid. Threads were dipped into this solution, then into a 0.6 per cent solution of sodium carbonate. They were then well rinsed in distilled water and dried for thirty minutes at 100°. This operation was repeated ten times. In one case the calcium carbonate was allowed to accumulate, while in another it was removed after each treatment by means of cold dilute acetic acid followed by rinsing in distilled water.

Original strength.....	1696
Calcium carbonate accumulated.....	1656
Calcium carbonate removed each time.....	1633

Two other series were treated with solutions of sodium sulfate, allowing the salt to crystallize out after removing the excess of solution as was done in the experiments with sodium carbonate. The threads were dried for thirty minutes at 100°, and rinsed well between treatments. Ten treatments were given each series.

Original.....	1696
5 per cent sodium sulfate.....	1584
10 per cent sodium sulfate.....	1614

These tests seem to indicate that this cannot be considered a large factor in the disintegration of laundered articles.

#### ACTION OF ACIDS

**MINERAL ACIDS**—Owing to the high price of oxalic and acetic acids it was thought advisable to determine whether or not cheaper acids could be substituted. Sulfuric and hydrochloric acids were chosen as the most desirable ones, and a series of tests was run to compare the harmful effects produced.

The test threads were dipped into *N*/50 (equivalent) solutions, wrung dry, as has been described above, then dried in an oven at 100° for thirty minutes. This was repeated ten times in each case, rinsing with distilled

water after each operation to remove the acid left in the threads.

Original strength.....	1717	Mean of (1706, 1680, 1718, 1716, 1767)
Acetic acid.....	1611, 1610	
Oxalic acid.....	682, 676	
Sulfuric acid.....	Less than 10	
Hydrochloric acid.....	Less than 10	

The results show clearly that the use of the cheaper acids should not be recommended for general adoption because the wash-room help cannot be depended upon to rinse sufficiently to remove the excess of acid employed. If the rinsing were sufficient, however, these strong acids might be used with entirely satisfactory results, as will be explained below.

#### USE OF ACID NECESSARY

It would seem that the use of acids might be dispensed with, or at least be made much less objectionable than at present. There are two facts, however, which seem to make the use of some acid indispensable. The small quantity of alkaline substances which is not removed by rinsing would have but little effect in weakening the fabric even if the articles were placed in the dry room or were passed over the heated rolls of an ironing machine. This alkali is objectionable, however, because it forms a bright yellow product with the oxycellulose which is produced by the action of the bleaching solution on the cellulose. Very small quantities of alkali are able to produce an undesirable color in a piece of bleached cloth, as will be shown later. Some acid is necessary, too, for the purpose of removing colored compounds of iron which are present as individual stains or as a general discoloration which results from the use of water or of supplies containing even small quantities of iron salts.

These tests indicate that by the use of acetic acid the damage done may be made almost negligible.

Acetic acid being a weak acid, that is one only slightly dissociated, yields relatively small concentrations of hydrogen as ion, and consequently the conversion of cellulose into hydrocellulose is effected by it less rapidly under corresponding conditions than when the stronger acids are used. The volatility of acetic acid also makes it less harmful than any of the other acids experimented with. It is interesting to note that the order in which the acids attack cellulose and decrease the breaking strength of the threads is the same as that in which they are found to be dissociated into their ions. In many localities, however, oxalic acid is the only substance which will remove the iron compounds sufficiently, and for this reason must be used. The troublesome iron compounds are either oxides or basic salts of iron, which are soluble in the presence of sufficiently large concentrations of hydrogen as ion. Oxalic acid possesses the additional property of forming a complex ion with iron as ion, and consequently is a more efficient solvent for these colored products than is acetic acid. Under these circumstances it has been found possible to effect an improvement by using acetic and oxalic acids together, using only as much oxalic as is required to correct the discoloration, and the acetic for making up the bulk of the acid. Careful rinsing is, of course, necessary in any case.



A series of threads was boiled in *N*/10 sulfuric acid for two and a half hours, and the final breaking strength was found to be 216. It is evident, then, that with the weaker solutions of the weaker acids used, and at the lower temperatures, the damage done while the articles are in the machine is not great.

#### POSSIBLE SUBSTITUTES FOR ACIDS

Acid sodium sulfate is a cheap substance which might be used for the acid bath. Theoretically, however, it offers little advantage over the use of sulfuric acid itself, because the concentration of hydrogen as ion from acid sodium sulfate is relatively large. This is so because sulfuric acid is a strong dibasic acid, and the bisulfate ion is, therefore, largely dissociated in weak solutions.

An acid sold under a trade name was analyzed and found to be commercial acid sodium sulfate. It was said to be absolutely harmless for laundry use. From the above considerations, this statement seemed very improbable. To test this assertion a series of threads was treated with an *N*/50 solution of the bisulfate in the same way that the experiments were made with the other acid solutions. The results show that the claims for this article were not founded upon fact.

Original breaking strength	1717
After ten treatments with <i>N</i> /50 bisulfate.	170

The bisulfate is somewhat less harmful than sulfuric acid, owing perhaps to the fact that the salt crystallizes out during the drying process. It is more conveniently handled than sulfuric acid, which is a liquid, but certainly the launderer should know that he is dealing with a very strongly acid substance, and not with some harmless acid, as is often claimed in advertisements.

#### BLEACHING

Since the bleaching is unquestionably the most

not only on the objectionable colored substances, but also upon the cellulose of the fabric, changing it into the brittle compound, oxycellulose. This formation of oxycellulose not only weakens the fibers to the extent to which they are thus attacked, but the oxycellulose is objectionable for a number of reasons. It is well known that oxycellulose is more readily dyed by basic dyestuffs than is cellulose itself, and for this reason any oxycellulose which is not removed is more deeply colored than the other parts. The behavior of oxycellulose in the presence of alkalies, which has been spoken of, is also a frequent source of trouble.

In order to determine whether or not this behavior is the cause for the yellowing of certain lots of clothes in the laundry and also of those which are stored after having been laundered, the following experiments were performed:

Some pieces of bleached muslin and of cambric were procured on the market and used as the test pieces. Parts of each of these were bleached to the extent of five treatments in the laundry, and parts to the extent of ten such treatments. Test pieces about three inches square were cut and treated as described below. The pieces were dipped into standard solutions of reagents and then the excess of the solution squeezed from them by hand. After standing at room temperature the pieces were examined at intervals to compare their color with that of the original untreated samples. The sizing was removed from all of the cloth by boiling in distilled water.

From these tests it is evident that the yellow color is greatest for a given concentration of the carbonate in the case of the pieces which have been most strongly bleached, that is, which contain most oxycellulose. The presence of even minute quantities of sodium carbonate is able in time to cause a very noticeable

EFFECT OF ALKALI ON COLOR

No.	KIND OF CLOTH	Strength of sod. carb. solution used	Time after removing from solution	Condition after treatment
1	Original muslin	<i>N</i> /10	3 hrs.	Slightly yellow
2	Muslin, bleached medium (Muslin A)	<i>N</i> /10	3 hrs.	Very yellow
3	Muslin, bleached strongly (Muslin B)	<i>N</i> /10	3 hrs.	Yellower than 2
4	Muslin B	<i>N</i> /10	rinsed 3 times with distilled water	
5	Original muslin	<i>N</i> /10	3 hrs.	Yellower than 1
6	Muslin A	<i>N</i> /10	3 hrs.	Less yellow than 1
7	Muslin B	<i>N</i> /10	3 hrs.	About like 2
8	Cambric, medium bleached (Cambric A)	<i>N</i> /10	3 hrs.	About like 3
9	Cambric, strongly bleached (Cambric B)	<i>N</i> /10	3 hrs.	Yellower than 6
10	Original muslin	<i>N</i> /50	16 hrs.	Yellower than 7
11	Muslin A	<i>N</i> /50	16 hrs.	Slightly yellow
12	Muslin B	<i>N</i> /50	16 hrs.	Much less yellow than 2
13	Original muslin	<i>N</i> /100	72 hrs.	Less than 3
14	Muslin A	<i>N</i> /100	72 hrs.	Slightly yellow
15	Muslin B	<i>N</i> /100	72 hrs.	Yellower than 1
16	Original cambric	<i>N</i> /100	72 hrs.	Yellower than 4
17	Cambric A	<i>N</i> /100	72 hrs.	Yellower than 4
18	Cambric B	<i>N</i> /100	after 52 days	Much yellower than blank
19	Muslin A	<i>N</i> /250	after 72 hrs.	Much yellower than blank
20	Muslin B	<i>N</i> /250	after 52 days	Much yellower
21	Original muslin	<i>N</i> /500	after 52 days	Much yellower than blank
22	Muslin A	<i>N</i> /500	after 52 days	Same as blank
23	Muslin B	<i>N</i> /500	after 52 days	Same as blank
24	Muslin B	<i>N</i> /1000	after 52 days	Yellower than blank
			after 82 days	Very little yellower than blank

harmful of all the parts of the washing process, and it seems impossible to produce a sufficiently white color to satisfy the trade when no bleaching agent is used, a great deal of experimenting was done with a view to improving this operation. The objection to the method now employed is that the hypochlorite solution acts

yellowing in articles which have been strongly bleached.

Test pieces which were treated with oxalic acid under varying conditions, some of which were boiled in *N*/10 oxalic acid for an hour, did not develop a yellow color even after the expiration of five months. This shows that no colorless compounds were formed

by reduction, which subsequently yielded the original colored substances by the oxidizing action of the air. The yellowing of articles on standing has often been attributed to this latter cause.

**BLEACHING IN SEPARATE SOLUTION**—For the purpose of determining whether or not it would be better to bleach in the second soap solution or in a separate solution after the washing was finished, the following experiments were performed.

A soap-alkali solution of about the strength used in the collar tests was heated to boiling. No cellulose was used in this test. Sufficient bleach solution was added to make the concentration of the hypochlorite the same as that used in the above tests. The boiling was continued after the addition, and the hypochlorite was found to have disappeared after 18 minutes. Another quantity of the bleach solution was diluted so that it had the same concentration as in the soap solution. The proper quantity of cellulose was weighed out and added, so that the ratio of the weights of the cellulose and the solution might be the same as in the previous tests on collars and threads. The boiling was continued and the hypochlorite found to have disappeared in about the same length of time as above—18 to 19 minutes.

A solution of the hypochlorite with no soap or cellulose was evaporated to dryness. Water was then added to redissolve the salts, the volume being made equal to that of the original solution. This process was again carried out and after the third evaporation a strong test for available chlorine was obtained. Lunge<sup>1</sup> has shown that a neutral solution of hypochlorite, or one which is slightly alkaline, can be boiled for two hours with a disappearance of only 24.6 per cent of the available chlorine. It is evident, therefore, that the hypochlorite reacted with the soap and the cellulose in the above tests, and was not decomposed by the high temperature to which it was subjected.

From these tests it was concluded that the soap was attacked by the hypochlorites about as readily as the cellulose, and if this were the case a smaller quantity of bleaching agent than that used with the soap should be able to do the same work if used separately. This was tried both in the laboratory and in several laundries, and besides a saving of from one-half to two-thirds of the bleaching material, better looking work was obtained in every case.

**REDUCING AGENTS** On account of the objectionable properties of oxycellulose, it was thought advisable to try the use of reducing agents instead of the oxidizing agents which are generally used. Sodium hydrosulfite was chosen as being the one most likely to give satisfactory results at a reasonable cost. Laboratory experiments showed that this substance when used in quantities chemically equivalent to the ordinary bleach solutions gave results that promised to be satisfactory. The best results were obtained when the hydrosulfite was used after the second suds, although a good color was obtained when the bleach

was used along with the soap. Although the cost of the hydrosulfite was high, it was considered possible to produce it at a sufficiently low price to justify its use if it proved satisfactory in other respects.

A test on a series of threads showed that very little decrease in their breaking strength was caused when they were boiled in relatively strong hydrosulfite solutions. The solution was made up 10 grams per gallon, and the boiling continued for two hours, to correspond to ten treatments.

Original strength.....	1696
Final strength.....	1685

This process was tried out on a large scale in two custom laundries. After a large number of runs it was found that although a considerable bleaching was effected, the color was not as good as when the old method was used. The quantities of hydrosulfite used for a hundred shirts (75 lbs. of cellulose) in twenty-five gallons of the solution were varied from 1/4 to 1 1/2 lbs. The bleaching effected by the smaller quantity was good, but owing to the fact that whiter work could be gotten by the use of hypochlorites the method was abandoned, as it was not thought likely to be generally accepted.

On account of the failure of the reducing agents to produce work that would compare in whiteness with that obtained in practice, attention was again turned to other oxidizing agents. It was hoped that an oxidizing agent might be found which would not attack cellulose as much as do the bleaches now in use, and which would effect the desired whitening of the article to be treated.

#### MAGNESIUM AND SODIUM HYPOCHLORITES

Magnesium hypochlorite was tried, as was also neutral sodium hypochlorite. Since the oxidation is caused by the hypochlorite ion, and the concentration of this was made the same with each of the hypochlorites, the only chance for a difference in their actions was the possibility that the concentration of hydroxyl ion might influence the reaction between cellulose and the hypochlorite ion. Since magnesium hydroxide is difficultly soluble, it is impossible for the magnesium hypochlorite solution to contain a large concentration of hydroxyl ion.

Many text books contain the statement that magnesium hypochlorite has a much less harmful effect on cotton and linen fabrics than calcium or sodium hypochlorites. A thorough search through the literature showed that this statement is copied from the patent specification submitted by Hermite,<sup>1</sup> concerning his process for preparing magnesium hypochlorite by electrolysis from a solution of magnesium chloride. No data are given in support of this statement in this patent specification, and none have been found in any other place.

Equal weights of threads were used with equal volumes of the different hypochlorites, which were made of equivalent strengths. The conditions of boiling the threads in all cases were the same.

Original strength.....	1696
Sodium hypochlorite.....	468, 488
Magnesium hypochlorite.....	474, 492

<sup>1</sup> English Patent 13,929, *J. Soc. Chem. Ind.*, 4, 673.

<sup>1</sup> *J. Soc. Chem. Ind.*, 4, 722; also, "Manufacture of Sulfuric Acid and Alkalies," second edition, Gurney and Johnson, London, 1896, pp. 417 and 419.

## OZONE FOR BLEACHING

Ozone is another oxidizing agent which was experimented with, and it was chosen because the only decomposition product which could be formed is oxygen and this, of course, is not objectionable. Preliminary tests indicated that the bleaching could be done satisfactorily, and if precautions were taken to prevent the simultaneous formation of oxides of nitrogen or to remove them if formed, the strength of threads was not greatly decreased after several successive treatments.

Original strength	1696
Exposed to current of ozone, oxides of nitrogen not removed	less than 5
Oxides of nitrogen removed by tower filled with slaked lime	575
Oxides removed by bubbling ozonized air through water	937

The percentage of ozone by volume was 1.2, and the temperature of the room 22.5° C. The time of passing the current of ozonized air was three and a half hours. The threads were introduced moist, about as they would have come from a laundry centrifugal machine. It could not be decided, however, by the use of the small laboratory apparatus whether the process was sufficiently economical and the bleaching action sufficiently rapid to be practical.

The laboratory ozonizer used was the regular Siemens-Halske apparatus, composed of five cells. By varying the rate of flow of the air it was possible to get a mixture which analyzed from 0.5 to 1.5 per cent by volume of ozone. The quantity of air thus furnished varied from 0.5 to 2 cu. ft. per hour. The concentration of the ozone was determined by titrating the iodine liberated by a known volume of ozonized air from a neutral potassium iodide solution. It was necessary to add acid to decompose any iodates which might have been formed before the titration was made with standard thiosulfate. A gas meter was connected ahead of the ozonizer to show the rate at which the air passed through the apparatus. The air was carefully dried with calcium chloride and concentrated sulfuric acid, in order to reduce the quantity of oxides of nitrogen formed.

The first plan tried was to pass the current of ozonized air into the drying room either before the drying was commenced or while it was in progress. To test this method some starched collars which had not been bleached previously were placed in a large glass desiccator through which the ozonized air was led. After half an hour, the color of the collars was very satisfactory, being better than that obtained in the usual way. When these collars were ironed, however, a very yellow color developed which was due, perhaps, to the fact that part of the starch had been converted into dextrine and this developed a yellow color at the high temperature because of the alkaline substance which had not been removed by rinsing. It was evident that this method could not be used unless the bleaching were done before the articles were starched. As this would necessitate an extra handling of the pieces, and would lengthen the time of treatment, the method was abandoned. The ozone was then used in a different way, which also gave satisfactory

results in regard to color. The current of ozonized air was led into the washer while the washing was being done. Tests were run on a series of threads which were boiled for five hours, with the same strength soap-alkali solution as was used in the tests described above, and a strong current of ozonized air passed through continuously. This corresponded to the effect of ten successive treatments such as were to be used in practice.

Original breaking strength	1696
After treatment	1389

In order to test the commercial efficiency of the latter method, a large ozonizer furnished by the Gerard Ozone Process Co. was installed in a custom laundry. The current of ozonized air was led into the washer by means of a perforated brass pipe, and allowed to bubble through the fabrics while they were being run in the machine. This large ozonizer was rated to furnish a current of air containing from 0.5 to 0.7 per cent ozone by volume at a rate of 25 cu. ft. per hour. Tests were run in which the ozone was admitted at all possible times during the regular washing process.

The results obtained when the ozone was passed into the soap-alkali solution were not satisfactory. Fruit and coffee stains were not removed sufficiently well to make the method serviceable. This was thought to be due in part to the fact that the ozone was largely decomposed by the hot water before it came into contact with the stains.

In order to overcome this difficulty, the ozone was used with the clothes in luke-warm water either before or just after the washing with soap was done. The color of the articles was not satisfactory in either case, although the passage of ozone was continued in some cases for forty minutes. Because of the expense of operating the apparatus, and also because of the length of time necessary to do the bleaching, the method was abandoned as not practical.

## ACTION OF HYDROGEN PEROXIDE

Some preliminary experiments were performed with hydrogen peroxide, but it was found that even with solutions of considerable strength the action was very slow. Very satisfactory results were obtained with hydrogen peroxide in bleaching woollens, and this method is being extensively used for treating fine woolen articles. The solution is made slightly alkaline with ammonia in the latter case.

## DISCUSSION OF USE OF BLEACH

The fact that colored articles last much longer than undyed ones made from the same kind of material, is proof that the use of excessive quantities of alkalies and bleach is responsible for the greater part of the damage done in the wash room. It is general experience that a colored shirt will outlast a white one by considerable, and the reason would seem to be that in the case of the colored shirt alkalies and bleaches must be used very sparingly or not at all.

A great advance would be made if all laundries used much less bleach than they do at present. If bleach is used once on a piece of fabric, it is necessary



to use it every time the article is laundered. This is because the oxycellulose formed the first time bleach is used yields the objectionable yellow substance already spoken of when alkalies are used subsequently, and the use of more bleach becomes necessary.

These experiments with bleaching agents seem to show that if excessive damage is to be avoided, some sacrifice in the color of the finished articles will need to be made. This might be accomplished either by using hydrosulfitcs, or other reducing agents, or by using much smaller quantities than are now considered necessary, of some of the oxidizing agents in use at the present time.

#### CONCLUSIONS

1—The bleaching and treatment of fabrics with acids are the most harmful parts of the process now in general use in steam laundries. The bleaching not only weakens the fabrics, but also produces oxycellulose, which yields an objectionable yellow substance when treated with even dilute solutions of alkalies. The hydrolysis of cellulose produced by the hydrogen as ion in acid solutions weakens the fibers. Thorough rinsing is essential to remove as much of the acid used as possible. The quantities of bleaching solution and acid used should be kept as small as possible.

2—The use of alkalies in excess affects prejudicially the color and strength of fabrics, and leads to the formation of much lint.

3—Contrary to the common belief of launderers, soft water is superior to hard water for all purposes, rinsing included.

4—The deposition in the fibers of insoluble salts or the crystallization of soluble salts does not greatly affect the wearing qualities of fabrics.

5—The use of mineral acids in the laundry cannot be generally recommended, because of the extent to which they attack cellulose if they are not thoroughly removed by rinsing.

6—One cause for the yellowing of fabrics composed of cellulose on standing is the formation of yellow products by the action of hydroxyl ions on the oxycellulose which is formed during the bleaching process.

7—A saving in the quantity of bleaching solution required and an improvement in the color produced are possible when the bleaching is done as a separate process. The usual practice is to combine washing and bleaching.

8—Hydrosulfitcs may be used for effecting the bleaching, but the color obtained is not as good as that produced by hypochlorites.

9—Magnesium hypochlorite solutions present no advantages over the slightly alkaline solutions of sodium hypochlorite now employed, as far as their destructive actions are concerned.

10—Ozone produces a satisfactory color when allowed to act on fabrics before or during the drying which is effected in the drying rooms. The fabrics are less attacked than in the present method, but the ozone process is not well received by the trade because it necessitates extra handling of the articles, and increases unduly the length of time necessary to complete the laundering operation.

### A PRACTICAL METHOD FOR THE PREPARATION OF DRY STARCH, SOLUBLE IN COLD WATER, FOR USE AS AN INDICATOR<sup>1</sup>

By ROBERT M. CHAPIN

Received April 18, 1914

When, several years ago, the necessity arose for preparing a large quantity of dry starch which should be readily soluble in cold water and appropriate for use as an indicator in iodine titrations, no description of a sufficiently practical method of preparation could be found.

Wroblewski<sup>2</sup> prepared the desired form of starch by running a concentrated solution of soluble starch, in a thin stream, and with vigorous stirring, into a large excess of alcohol, followed by washing with absolute alcohol and ether, and drying *in vacuo*. He stated the resulting product to be soluble in cold water up to about 4 per cent, and to yield a pure blue with iodine. His original soluble starch was prepared by digesting rice starch with 1 per cent caustic potash solution.

In the present work, Wroblewski's method of precipitation, etc., was found effective, but for the preparation of the original soluble starch, Lintner's<sup>3</sup> method of digestion with acid proved more satisfactory. The first preparations, made in 1911, were of good quality, but were obtained through a series of tedious and expensive processes. Since that time, through the repeated preparation of large quantities of the material, the process has become so simplified and standardized that it is believed to be worthy of publication.

Into a 5-liter round flask with a long neck are brought 400 grams potato starch, 2300 cc. distilled water, and lastly, 80 cc. normal hydrochloric acid. The flask is well shaken to wet and distribute the starch thoroughly, and is floated in a kettle of water previously brought to vigorous boiling. The neck of the flask rests conveniently on the side of the kettle at an angle of about 45°, and as soon as the flask is brought into the bath it is smoothly and continuously rotated about its longitudinal axis. As the flask becomes hot the starch forms an evenly distributed uniform jelly, which, in about seven minutes from the time of starting, begins to liquefy and to fall away from the wall of the flask. When this stage is reached the mouth of the flask is loosely closed with an inverted beaker and the flask left in the boiling bath with an occasional rotation until the mobile liquid shows no lumps of gelatinized starch remaining—1 to 1½ hours. The flask is then rapidly cooled in running water until it can be comfortably handled (about 50° C.), then methyl orange is added, followed by concentrated ammonia to alkaline reaction. Next is immediately added 800 cc. of 95 per cent alcohol, and, after thorough mixing and standing for a few minutes to allow air bubbles to separate, the liquid is strained through moderately coarse muslin. The addition of this proportion of alcohol notably reduces the viscosity and increases the permanence of the solution. Starch will separate some time after the solution has become cold, but with proper management ample time remains for the subsequent operations. In fact,

<sup>1</sup> Printed by permission of the Secretary of Agriculture.

<sup>2</sup> Ber., 30 (1897), 2108.

<sup>3</sup> J. für prakt. Chem., 34 (1886), 378.

after experience has been gained, the amount of water, and in due ratio the total amount of alcohol, may be somewhat reduced. The solution, still at 40 to 45° C., is run through a number of fine jets into four liters of 95 per cent alcohol, with continuous stirring. The whole is left for at least 48 hours with an occasional thorough stirring after which most of the supernatant alcohol is decanted and the rest used to transfer the starch to a two-quart percolator provided with a filter plate which is covered with filter paper or cloth. Here it is percolated with 95 per cent alcohol, being stirred up with a stick at intervals to prevent the formation of clumps or fissures, until alcohol comes through the percolator of a specific gravity indicating a strength of 90 per cent. The starch is then transferred to a Buchner funnel, well drained with suction and spread out to dry in a moderately warm place.

The resulting product is a fine white voluminous powder, more or less compacted to friable lumps which completely disintegrate under slight pressure. In less than a minute, a little of it thrown into cold water dissolves sufficiently to yield a good blue upon the addition of potassium iodide and iodine. Moistened with water or dilute alcohol, it becomes gummy and subsequently dries out to a horny mass, very slowly soluble in cold water. The efficiency of the preparation, therefore, resides largely in its fine state of subdivision and care must be taken during the process of preparation not to expose it to air until after thorough digestion with alcohol of 90 per cent strength. After drying it should be preserved from moist air, though it is not injured by exposure to ordinary atmospheric conditions.

The advantages of the material for iodine titrations made in the field with a portable outfit are sufficiently obvious. It is also a very convenient substance to have about a laboratory, although for highly accurate titrations it is somewhat inferior in sensitiveness and delicacy to a properly prepared fresh solution made from raw starch.

Since the above described process was worked out, Fernbach<sup>1</sup> has described very similar observations; namely, that a dilute starch paste or solution run in a fine stream into a large excess of absolute alcohol or acetone, produces a finely divided precipitate which is soluble in cold water. He apparently attributes the soluble qualities of the resulting product to the dehydrating action of the alcohol or acetone. Inasmuch as the horny form of precipitated starch previously mentioned, and indeed raw starch as well, becomes soluble in cold water when finely ground, the present writer believes that the prime factor which determines the readiness with which precipitated starch dissolves in water is simply the degree of fineness of its mechanical subdivision. It was early found that the more dilute the original starch solution and the greater the excess of alcohol, the finer, more voluminous and more readily soluble in water became the resulting product, but naturally, the less practical became the process.

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<sup>1</sup> Original Communications, Eighth International Congress of Applied Chemistry, 13 (1912), 131.

## DETERMINATION OF SILVER AND BASE METAL IN PRECIOUS METAL BULLION<sup>1</sup>

By FREDERIC P. DEWEY<sup>2</sup>

Received May 18, 1914

The determination of silver in gold bullion by cupellation methods is such a simple matter and so easily executed that it has long been the standard and almost universally accepted method, but the investigations described in this paper show that it has most serious and incurable defects. In making an assay of gold bullion for base metal, which is the basis for the silver determination, the base metal is not entirely removed from the button, and no means are at present available for insuring the presence of even approximately the same amount of remaining base metals in duplicate buttons. The judgment of the cupeller is the only guide in the matter. The amount of gold and silver absorbed by the cupel may vary greatly in duplicates. The proofs are subject to the same variations as the assays, and it is purely a matter of chance whether they give the proper correction figures or not, and they may fall far short of doing so.

These difficulties are inherent in the work of any one assayer, but when different assayers work upon the same sample, particularly in different laboratories, the opportunities for variation are multiplied; when they work upon different samples of the same bullion, there is no telling how widely they may differ in their reports, even upon apparently docile bullion.

There is urgent need for a better method, but a thoroughly better one is not yet available and undoubtedly the cupellation method will remain in use for many years to come. This paper further describes an attempt to establish a better method by means of fusion with cadmium and titration with sulfocyanate, which, while not entirely successful, is very promising. Comparative tests by cadmium fusion and Gay-Lussac titrations are also described.

During the fiscal year ended June 30, 1912, the Mint service of the United States Treasury purchased 74,179 deposits and redeposits of bullion, most of which contained more or less silver. In the vast majority of cases the fineness of the silver in the bars was not determined directly, but by a method of differences based upon cupellations by which the fineness of gold and base metal present were determined, the difference between these two actual determinations and 1000 being called the silver fineness.

There are two general methods of arriving at the silver result. The actual assaying work in both cases is the same, but the methods of calculating the results differ. In both of them the gold fineness is first determined by a separate assay. Then, in one method of calculating, the combined gold and silver fineness are determined by a second assay and the gold figure subtracted from the combined gold and silver figure to give the silver fineness. In the second method of calculating, the result of the second cupellation is stated as the loss on cupellation, or base metal, and the sum of this determination and the gold determination is subtracted from 1000 to give the silver fineness.

<sup>1</sup> Published by permission of the Director of the Mint.

<sup>2</sup> Assayer, Bureau of the Mint.

Many of these deposits were purchased at the smaller assay offices of the United States, scattered all over the country, and were subsequently shipped to the larger offices to be refined. These larger offices necessarily treated the smaller ones just as though they were outsiders, making their own weights and assays and often remelting the bullion before accepting the bar. Naturally there are at times differences between purchasing and redeposit offices. Taking the figures of the purchasing offices as a basis, Table I shows the relation between the silver determinations of the purchasing offices and those of the redeposit offices upon 579 redeposits last year which were not remelted at the redeposit offices. It gives the number of times they agreed in their silver determinations and the number of times they differed in fineness by the amount stated.

TABLE I SILVER ASSAYS ON 579 REDEPOSITS

TABLE 1. SILVER ASSAYS ON 977 REDEPOSITS																					
Redeposit office agreed with purchase office.....																					59
Redeposit office differed from purchase office.....																					520
Difference in fineness.....																					
Above.....	1	12	1	11	2	20	3	31	4	41	8	81	6	61	7	8	81	10	101	12	
Below.....	57	56	44	38	32	21	12	11	5	6	6	2	2	4	1	1	4	1	1	294	
Totals.....	101	115	87	69	53	28	18	11	9	6	7	2	2	4	1	1	4	1	1	520	

From Table I it is apparent that the general tendency of the redeposit office is to get higher results on the silver than the purchasing office. It is barely possible that a very few of the results at one redeposit office were not obtained by cupellation.

Of course, some of the differences shown are due to differences in the samples used for the assay work, but the differences are still much too large in many cases and call for improvement in the assaying or for the substitution of some other method for determining the silver.

It is evident that the silver result is naturally open to considerable variation, because its accuracy is dependent upon the accuracy of the two determinations which are actually made. When the net errors of the two actual determinations are opposite it may happen that the silver figure will be close to the truth, but when they are both on the same side the error in the silver determination may be quite large.

I have published two papers<sup>1</sup> dealing with the accuracy of the determination of gold in bullion, showing that the accuracy often claimed for this determination is not generally obtained and that in some bullions the gold determination cannot be depended upon within one fine. In the presence of certain elements, such as arsenic and antimony and in the case of very impure bullion, such as some cyanide bars and some jewelry scrap, the gold assay is subject to much wider variations and is entirely unsatisfactory of itself, to say nothing of its baneful influence upon the silver determinations by cupellation differences.

The cupellation for base metal in gold bullion is a ridiculously simple operation and may be described in a very few words. The assay sample of the bullion is weighed, wrapped in the proper amount of sheet lead and cupelled, accompanied by the proper proofs, to a button of gold and silver, which is cleaned and

weighed. The difference between the weight of the button of gold and silver, when corrected by the proof, and the sample taken, is called base metal that has been driven off or absorbed by the cupel. Aside from carelessness, there appear to be but few chances for variation in the operation, but I shall show that some of these chances are exceedingly potent.

It is a fair assumption that the chances of error in weighing the assay sample and the resulting button will be approximately the same as in weighing the sample and cornet in the gold assay. In view of the wide errors that may occur further on in the work it is safe enough to put down the vitiation of the silver determination from this cause as being negligible for the present.

In the actual cupellation in the furnace for removal of the base metal, the first point to attract attention

as bearing upon the chances for loss and variation in the result is the possible volatilization of the precious metals during cupellation. Much has been written upon this subject, but most, if not all, of the numerical conclusions announced have been based upon either insufficient data, or upon tests made under conditions which do not at all occur in actual assaying. There is no question that gold and silver are volatile at sufficiently elevated temperatures, but it is an open question how much they do volatilize in actual assaying. It is still more uncertain as to whether it is necessary to carry on the assay work under conditions which produce or even favor the volatilization of the precious metals.

It is by no means an easy matter to obtain the data required to answer this question with any certainty. It is necessary to know the amount of precious metal going into the assay, the amount absorbed by the cupel and the amount actually remaining in the final button as weighed. This last determination requires much careful and painstaking analytical work. As a practical fact, the only way to arrive at this figure is to make wet determinations, with special precautions, of the other metals remaining in the buttons and then call the balance precious metals. I have done considerable work of this character and am in the habit of speaking of it as "hen's-tooth" analysis. I have made several attempts to determine the volatilization loss in the cupellation assay for gold only, but the results obtained are unconvincing and their value seems hardly commensurate with the labor involved. After going through the work, one may get a figure showing a slight loss which may be due to volatilization, but it will be loaded with all the errors of a large amount of analytical work. On the other hand it may easily happen that a slight gain will be shown.

My personal opinion is that in the vast majority of cases and with the exception of bullion high in copper and certain exceptional classes of bullion, such as those containing arsenic and antimony, the volatiliza-

<sup>1</sup> "The Assay and Valuation of Gold Bullion," *Trans. A. I. M. E.*, **40**, 780. *Ann. Rept., Director of the Mint, 1908-9*, p. 25. "The Sampling of Gold Bullion," *Trans. A. I. M. E.*, **44**, 853. *Orig. Com., 8th Int. Congr. Appl. Chem.*, **1**, 155.



tion of precious metals in properly conducted base metal assays is insignificant.

The Bureau records contain various cases of excessive loss in base metal proofs which might seem to indicate volatilization of gold and silver during the cupellation, but in the cases where the cupels have been assayed, as far as the records now show, the absorption of precious metals by the cupels has always been more than sufficient to account for the high-proof loss, so that it is by no means necessary to turn to volatilization to explain the excessive loss of the proofs. Specific illustrations of this will be given further along.

It has been known for a very long time that the button obtained in the base-metal assay is by no means pure gold and silver. The work of Tillet (1761-1769) showed that the weight of a silver cupel button added to the weight of silver absorbed by the cupel exceeded the weight of the silver taken in test cases and that the excess was made up of copper and lead retained by the button. It has been stated on the authority of Tillet and D'Arcet that 1000 parts of a silver button may contain 4 parts of foreign metals. As already explained, when treating of volatilization, the accurate determination of the very small amount of copper and lead in a base metal assay button presents unusual difficulty. On one occasion, however, I had an accumulation of base buttons from two laboratories sufficient in amount to work with comfortably. One set was from the assaying of a single sample of standard gold and the other was from assaying three closely related samples of standard gold. I found much more than 4 parts of copper and lead, per 1000 parts of button. In both cases the bullion was only about 2 fine in silver, and 98 fine in copper, so that the work is not strictly comparable with Tillet's. The following results were obtained:

BASE METAL REMAINING IN CUPEL BUTTONS			
Mg. per gram			
	First laboratory	Second laboratory	
Lead.....	3.09	2.04	
Copper.....	12.62	20.84	

On various occasions I have examined the nitrate of silver solutions resulting from parting gold coin assays in sets in the Bureau laboratory. The gold and silver buttons in the gold assays may be treated as quite similar to the base-metal assay buttons, although not strictly the same, and by analyzing the solution from a set of assays there was sufficient lead and copper to work with. It is not possible to state the relation between the lead and copper retained and the weight of the buttons exactly, because neither the parting silver nor the buttons were weighed. In each case, however, the buttons weighed approximately 1450 mg. each. In six cases of regular work the proportion of both lead and copper retained by the buttons was much less in most instances than in the base buttons given above, the average amounts retained per button being as follows:

LEAD AND COPPER RETAINED BY GOLD ASSAY BUTTONS					
AVERAGE PER BUTTON OF APPROXIMATELY 1450 MG.					
Lead	Mg.	Copper	Mg.	Lead	Mg.
0.51		1.43		0.99	
0.84		1.18		1.06	
0.89		1.65		1.63	
				1.12	
				1.73	
				2.36	

In five cases the assays were intentionally run at an unusually low temperature and the retention of lead and copper was greatly increased as shown by the following results:

LEAD AND COPPER RETAINED BY GOLD ASSAY BUTTONS			
AVERAGE PER BUTTON OF APPROXIMATELY 1450 MG.			
Lead	Mg.	Copper	Mg.
1.252		6.789	
1.511		7.344	
1.533		6.98	
2.179		7.79	
2.626		8.167	

In the case of a set of fine gold assays the buttons weighed approximately 1625 mg. each and they averaged to contain 0.38 mg. lead and 2.07 mg. copper.

Since writing the above, Liddell,<sup>1</sup> in comparing bone ash with cement cupels, has uttered a timely warning against assuming the cupel bead to be free from base metals.

When, however, we take up the question of the cupel loss, or absorption, the case becomes quite different. At this point there are opportunities for wide variations which may be readily determined. These variations not only affect the results obtained by different assayers when working upon the same bullion, but they also affect duplicate assays by one worker.

In considering the question of loss of precious metals in the cupel, some sharp distinctions should be drawn, although they cannot yet be rigidly applied. There is a true and actual absorption of these metals into the body of the cupel, which may easily be demonstrated by filing off a portion of the used cupel far away from the button of metal and assaying it. There is an entanglement of one or more individual beads, often plainly visible, upon the surface of the cupel. There may also be a shower of microscopic beads scattered over a portion of the surface of the cupel. In the course of my investigations I have assayed several thousand cupels that have been made and used under most varied conditions, and hope soon to publish the results. At this time I propose to deal with the general aspect of the cupel in a brief manner only, as directly applicable to the base-metal assay.

The true absorption of a cupel depends upon a wide variety of conditions. The entanglement of individual beads may be due to the character and composition of the ash or the manufacture of the cupel or it may be due to imperfections in wrapping the assay sample in the sheet lead in making up the package or packet. A rain of microscopic beads in the cupel may be due either to the composition of the bullion or the temperature of the muffle. It may also possibly be due to the presence of an undue amount of salt in the bone ash.

It is a good plan to form the habit of always examining the used cupels for beads and when there is a wide difference between duplicate assays, such an examination is essential for good work. Whenever beads, either individual or microscopic, appear in a cupel, it must rest in the judgment of the assayer whether he will accept the original result or repeat the work. The amount of the true absorption is not visibly shown

<sup>1</sup> *Eng. Min. J.*, 96 (1913), 7.

by the cupel and can be determined only by assaying the used cupel. There is seldom sufficient time to do this in a busy commercial laboratory and it is generally assumed that it will be properly corrected by the proof. This, however, is often not even approximately true. Two cupels of identical manufacture standing side by side in the muffle may show wide differences in the amount of gold and silver absorbed when the same bullion is run in them and there are many cases where the proof is only approximately like the bullion being assayed, while such differences may materially affect the relative absorptions. When the cupels are separated in the furnace the differences may be augmented.

Some illustrations to show the effect of cupel absorptions in every-day work may be given. In these the figures stated are intended to represent true absorptions except as noted. Some of the illustrations are taken from actual commercial assaying for the purpose of showing the real conditions. Some of them are from regular work, which was, however, carried out so as to illustrate and investigate some particular point in the routine work, while some few are from specific investigating tests.

In one of the small offices the cupel absorption of gold and silver in duplicate base-metal assays of the A sample were 2.62 and 2.68 mg., but on the B sample they were 1.63 and 1.87 mg.<sup>1</sup> On another bullion the absorptions were 3.75 and 3.95 mg. On a third they were 4.81 and 6.03 mg. This is a most excellent illustration of every-day assaying. There was absolutely no discretion used in selecting the cupels to be assayed. They represent a run of assays on a day when the writer happened to be making an examination of the institution.

The cupels from the base-metal assays of five deposits at another small office were forwarded to the Bureau and assayed there, showing the following absorptions:

Fineness of bullion	Sample	Gold	Silver	Total
Gold 905.5.....	A	1.00	1.01	2.01
Silver 92.0.....	B	0.94	0.97	1.91
Base 2.5.....				
Gold 826.....	A	1.19	1.19	2.38
Silver 119.....	B	1.11	1.45	2.56
Base 85.....				
Gold 786.25.....	A	1.02	1.42	2.44
Silver 121.5.....	B	1.16	1.60	2.76
Base 92.25.....				
Gold 608.....	A	0.57	3.35	3.92
Silver 319.5.....	B	0.50	3.12	3.62
Base 72.5.....				
Gold 537.5.....	A	0.54	4.30	4.84
Silver 440.5.....	B	0.53	3.99	4.52
Base 22.....				

The general conditions in one of the largest laboratories in the service are illustrated by Table II which gives the cupel absorptions in base-metal assays on a wide range of bullions.

<sup>1</sup> For convenience in the Mint service a special set of assay weights is employed, known as "gold weights" and generally designated as "GW," based upon 500 mg. equal to 1000 GW so that 1 mg. equals 2 GW. In general 1000 GW of bullion are used for making a base-metal assay, so that the GW of the button as weighed gives the fineness of the bullion assayed. In a few cases in the paper it is noted that only a half charge, or 500 GW, was employed for the assay. In considering the data in this paper it should be remembered that 1 mg. means 2 in the fineness on a full charge and 4 on the half charge.

TABLE II CUPEL ABSORPTIONS (MG.) BASE-METAL ASSAYS IN LARGE LABORATORY

Gold	Silver	Total	Gold	Silver	Total
0.97	0.78	1.75	0.81	2.24	3.05
0.75	1.07	1.82	1.02	2.13	3.15
1.13	0.85	1.98	1.65	1.57	3.22
1.58	0.58	2.16	1.75	1.76	3.51
1.17	1.04	2.21	1.64	1.91	3.55
1.06	1.25	2.31	1.70	1.94	3.64
1.34	0.97	2.31	1.51	2.15	3.66
0.91	1.43	2.34	1.05	2.62	3.67
1.01	1.38	2.39	1.81	1.97	3.78
1.09	1.36	2.45	1.58	2.24	3.82
0.28	2.25	2.53	1.95	1.88	3.83
1.03	1.51	2.54	1.63	2.36	3.99
1.26	1.36	2.59	0.42	3.50	4.01
0.90	1.72	2.62	1.93	2.10	4.02
1.08	1.73	2.81	2.10	2.15	4.25
1.12	1.78	2.90	2.24	2.27	4.51
			2.49	4.32	6.81

These cupels were made on a power press from bone ash of the following screen composition:

On 40 mesh.....	4.75 per cent
On 60 mesh.....	10.75
On 80 mesh.....	23.0
On 100 mesh.....	7.5
Through 100 mesh.....	54.0
	100.00 per cent

A bullion high in copper that was very troublesome to assay and the composition of which is given approximately only at 457 fine in gold and 160 fine in silver yielded the following cupel absorptions in a set of base-metal assays using 10 grams of lead:

Gold	Silver	Total
3.48	3.49	6.97
3.90	3.68	7.58
5.74	4.17	9.91
6.14	4.29	10.43

As a general illustration of what may occur with a rain of microscopic beads, accompanied in some cases by separate beads, six such cupels that had been used in a purchasing office were assayed at the Bureau with the following results:

Gold	Silver	Total	Gold	Silver	Total
3.55	2.49	6.04	3.28	2.34	5.62
2.98	3.13	6.11	2.81	4.87	7.68
3.45	2.68	6.13	2.16	4.56	6.72

Five base-metal assays each were made on two high-grade bullions, accompanied by two proofs. The cupels were made on a hand-lever machine from the same bone ash as the cupels of Table II. The cupels were arranged in the muffle in three rows of four with the proofs in Nos. 2 and 3 of the middle row. The cupels showed the following absorptions:

COMPOSITION	Gold	Silver	Total
NO. 1 BULLION:			
Gold 898.5 fine	1.86	1.08	2.94
Silver 89.0 fine	1.97	1.02	2.99
Base 12.5 fine	2.21	1.10	3.31
	2.54	1.19	3.73
	2.48	1.19	3.67
NO. 2 BULLION:			
Gold 895.5 fine	2.02	1.03	3.05
Silver 98.5 fine	1.74	1.09	2.83
Base 6 fine	2.12	1.24	3.36
	2.42	1.30	3.72
	2.60	1.29	3.89
PROOFS:			
Gold 450 mg.	2.22	1.06	3.28
Silver 45 mg.	2.36	1.18	3.54

Two somewhat similar bullions from the same office were treated in the same way with the following results:

COMPOSITION 1ST BULLION:	CUPEL ABSORPTIONS (MG.)		
	Gold	Silver	Total
Gold 823.0 fine	1.18	1.48	2.66
Silver 164.25 fine	1.29	1.72	3.01
Base 12.75	1.44	1.69	3.13
	2.01	2.13	4.14
	1.99	1.91	3.90
2ND BULLION:			
Gold 884 fine	1.29	1.12	2.41
Silver 113.5 fine	1.32	1.07	2.39
Base 2.5	1.62	1.27	2.89
	1.99	1.37	3.36
	2.35	1.50	3.85
PROOFS:			
Gold 425 mg.	1.73	1.58	3.31
Silver 70 mg.	1.49	1.60	3.09

The cupels were made on a hand-lever machine from bone ash of the following composition:

On 40 mesh	None
On 60 mesh	10 per cent
On 80 mesh	24
On 100 mesh	59.5
Through 100 mesh	100.0

Eight samples of miscellaneous bullion were cupelled in duplicate at one time upon a plate in one of the large offices, the duplicates being widely separated in the furnace. The used cupels were assayed at the Bureau and showed the following absorptions:

TABLE III—MISCELLANEOUS BULLION CUPEL ABSORPTIONS (MG.) IN ONE SET

COMPOSITION	ASSAY	Gold	Silver	Total
Gold 350	1st	2.09	2.44	4.53
Silver 120	2nd	1.23	1.86	3.09
Base 530				
Gold 440	1st	1.57	1.94	3.51
Silver 150	2nd	1.41	2.11	3.52
Base 410				
Gold 520	1st	1.35	1.56	2.91
Silver 140	2nd	1.90	1.74	3.64
Base 340				
Gold 530	1st	1.09	1.99	3.08
Silver 210	2nd	1.34	2.19	3.53
Base 260				
Gold 690	1st	1.03	0.96	1.99
Silver 100	2nd	1.69	1.23	2.92
Base 210				
Gold 800	1st	1.03	0.91	1.94
Silver 120	2nd	1.30	1.05	2.35
Base 80				
Gold 890	1st	1.94	0.58	2.52
Silver 20	2nd	1.32	0.49	1.81
Base 90				

Along with these, two samples were run side by side, but the duplicates were cupelled in a different make of cupel, also side by side and separated from the originals on the plate. The used cupels gave the following absorptions:

CUPEL ABSORPTIONS (MG.)		BULLION IN DIFFERENT CUPELS		
COMPOSITION	CUPEL	Gold	Silver	Total
Silver 190	1st	1.39	2.17	3.56
Base 350	2nd	1.59	2.38	3.97
Gold 440				
Silver 180	1st	1.40	2.17	3.57
Base 380	2nd	1.59	2.22	3.81
Gold 460				

Eight base-metal assays were made in duplicate on various samples of a bullion, a proof being placed between each pair of duplicates, and the following absorptions (Group I) of gold and silver were shown by the cupels.

Other samples of the same bullion assayed in a different cupel and slightly hotter part of the muffle yielded the absorptions given as Group II:

GOLD AND SILVER ABSORBED (MG.)			GOLD AND SILVER ABSORBED (MG.)		
GROUP I			GROUP II		
1st Assay	Proof	2nd Assay	1st Assay	Proof	2nd Assay
1.55	1.71	1.75	2.18	2.26	2.00
1.73	1.88	1.76	2.23	2.36	2.46
1.81	1.82	1.75	2.19	2.41	2.35
1.80	1.88	1.76	2.32	2.44	2.28
2.43	2.47	2.42	2.96	3.11	3.10
2.37	2.66	2.44	3.22	3.26	3.00
2.67	2.66	2.61	3.34	3.28	3.16
2.67	2.62	2.60	3.41	3.60	3.14

This bullion was 757 fine in gold, 196 fine in silver and 47 fine in base. The cupels were made in a hand-

lever machine from bone ash of the following screen analysis:

	1st Cupel	2nd Cupel
On 40 mesh	1.0 per cent	1.25 per cent
On 60 mesh	2.5	11.00
On 80 mesh	6.0	21.50
On 100 mesh	13.5	17.75
Through 100 mesh	83.0	52.50
	100.0 per cent	100.00 per cent

Two other comparisons on a different bullion were similar to the last two runs, but the relative positions of the cupels were reversed and in this comparison No. 1 cupel was run slightly hotter than No. 2.

GOLD AND SILVER ABSORBED (MG.)					
HOTTER RUNS ON NO. 1 CUPEL			COOLER RUNS ON NO. 2 CUPEL		
1st Assay	Proof	2nd Assay	1st Assay	Proof	2nd Assay
1.98	2.27	1.97	1.97	2.13	1.89
2.16	2.30	2.14	2.00	2.07	2.07
2.33	2.66	2.37	2.21	2.31	2.18
2.72	2.96	2.91	2.46	2.76	2.98
2.84	2.85	2.90	2.60	2.53	2.51
3.07	2.99	3.00	2.66	2.53	2.51
3.17	3.34	3.30	2.76	2.64	2.77
3.27	3.22	3.05	2.86	2.74	2.72

This bullion was 712 fine in gold, 202 fine in silver and 86 fine in base.

Four sets of quadruplicate assays were made on various samples of a bullion, a proof being used between each two assays, making six cupels in each set, arranged in two rows of three in the furnace, and the following absorptions were shown:

GOLD AND SILVER ABSORBED (MG.)					
Assays	Proof	Assays	Assays	Proof	Assays
FIRST SET			THIRD SET		
2.44	2.34	2.44	2.49	2.52	2.38
2.82	2.72	2.67	2.82	2.61	2.22
SECOND SET			FOURTH SET		
2.36	2.35	2.38	2.55	2.93	2.54
2.72	2.81	2.67	3.04	2.82	2.96

In each set the first row of figures represents the front row of cupels in the furnace. This bullion was 770 gold, 214 silver and 16 base. The cupels were made on a hand-lever machine from bone ash of the following screen composition:

On 40 mesh	1.00 per cent
On 60 mesh	4.25
On 80 mesh	12.75
On 100 mesh	10.0
Through 100 mesh	72.0
	100.00 per cent

Two sets of samples of miscellaneous bullion were run in different cupels, with the following results:

TABLE IV—GOLD AND SILVER ABSORBED (MG.) MISCELLANEOUS BULLION

COMPOSITION	1ST CUPEL			2ND CUPEL		
	Gold	Silver	Total	Gold	Silver	Total
Gold 742.5	0.62	0.90	1.52	0.91	1.23	2.14
Silver 161.5	0.67	0.91	1.58	0.98	1.21	2.19
Base 96	0.71	0.90	1.61	1.03	1.48	2.51
	0.70	1.19	1.98	1.06	1.38	2.44
	0.82	1.05	1.87			
	0.94	1.19	2.13			
	1.06	1.30	2.36			
	1.09	1.28	2.37			
Gold 559	0.29	2.12	2.41	0.41	2.31	2.72
Silver 405	0.36	2.53	2.84	0.51	2.67	3.18
Base 36	0.49	2.88	3.37	0.54	3.98	4.52
	0.50	2.90	3.40	0.60	3.00	3.60
				0.72	3.52	4.24
				0.71	3.60	4.31
Gold 486.25	0.37	3.60	3.97	0.38	3.36	3.74
Silver 471.0	0.35	3.01	3.36	0.29	1.98	2.27
Base 42.75	0.36	3.86	4.22	0.41	3.33	3.74
	0.59	3.72	4.31	0.43	3.50	3.93
				0.51	3.74	4.25
				0.51	3.85	4.36
Gold 245	0.10	4.06	4.16	0.15	4.73	4.88
Silver 666	0.11	4.24	4.35	0.17	5.44	5.61
Base 89	0.13	4.78	4.91	0.18	5.32	5.50
	0.17	4.98	5.15	0.19	4.70	4.89
				0.20	3.65	3.85
				0.20	5.16	5.36
Gold 242.75	0.09	3.68	3.74	0.13	4.53	4.66
Silver 675.0	0.10	3.56	3.66	0.14	4.56	4.70
Base 82.25	0.16	4.93	5.09	0.15	3.24	3.39
				0.15	4.96	5.11
				0.16	4.55	4.71
				0.17	5.31	5.48



These cupels were made on a hand-lever machine from bone ash of the following screen composition:

	No. 1 Cupel	No. 2 Cupel
On 40 mesh.....	1.50 per cent	9.25 per cent
On 60 mesh.....	2.75	9.25
On 80 mesh.....	7.00	22.00
On 100 mesh.....	8.50	14.00
Through 100 mesh.....	80.25	54.75
	100.00 per cent	100.00 per cent

A cyanide bullion 884 fine in gold, 6 in silver and 110 base, being mainly zinc and cadmium, with practically no copper, yielded the following absorptions:

TABLE V—GOLD AND SILVER ABSORBED (MG.) CYANIDE BULLION					
Gold	Silver	Total	Gold	Silver	Total
0.79	0.07	0.86	0.91	0.09	1.00
0.81	0.06	0.87	0.92	0.11	1.03
0.82	0.09	0.91	0.98	0.07	1.05
0.82	0.09	0.91	1.01	0.08	1.09

This cupel was made on a hand-lever machine from bone ash of the following screen composition:

On 40 mesh.....	Slight trace
On 60 mesh.....	6.00 per cent
On 80 mesh.....	11.75
On 100 mesh.....	10.0
Through 100 mesh.....	72.25
	100.00 per cent

A very low-grade bullion, 110 fine in gold, 52 in silver and 838 base, which was mainly lead, yielded the following absorptions in the same cupel as that used in the above cyanide bullion:

TABLE VI—GOLD AND SILVER ABSORBED (MG.)—VERY LEADY BULLION

Gold	Silver	Total
0.28	0.83	1.11
0.29	0.58	0.87
0.33	0.81	1.14
0.37	0.49	0.86

The Mint service does not pay for silver where it is less than 8 fine in the bullion. The cupels used on three such bullions showed the following absorptions:

CUPEL ABSORPTION (MG.)

COMPOSITION		COPPER ABSORPTION (MG.)		Gold	Silver	Total
No. 1 BULLION:						
Gold	892.25 fine....	Proof	A			2.28
Silver	7.5 fine.....		B	2.25	0.19	2.44
Base	100.25.....					
No. 2 BULLION:						
Gold	988.25.....	987	A	1.80	0.23	2.03
Silver	6.5.....	13	B	1.91	0.12	2.03
Base	5.25.....		Proof	1.88	0.13	1.94
No. 3 BULLION:						
Gold	985.75.....	987	A	1.84	0.11	1.95
Silver	7.0.....	13	B	2.14	0.11	2.25
Base	7.25.....		Proof	2.05	0.15	2.20

A fourth bullion was assayed in three different cupels, but unfortunately I do not know the screen composition of the ashes used. The following absorptions were shown:

CUPEL ABSORPTION

		No. 1 CUPEL				
COMPOSITION			Gold Mg.	Silver Mg.	Total Mg.	
Bullion		Proof	A	2.19	0.15	2.34
Gold	987.75	990	B	1.70	0.12	1.82
Silver	6.0	5	Proof	2.15	0.09	2.24
Base	6.25	5				
		No. 2 CUPEL				
			A	1.38	0.10	1.48
			B	1.42	0.13	1.55
			Proof	1.17(?)	0.29	1.46
			A	1.81	0.09	1.90
			B	2.02	0.12	2.14
			Proof	1.99	0.18	2.17

A special series of synthetic alloys or proofs containing 8 and 10 GW silver and varying amounts of gold and copper were cupelled with varying amounts of lead at one of the mints and the used cupels were assayed at the Bureau. Table VII summarizes the data. The column "Button losses" gives the basis for the corrections that would have been applied to the base metal determinations if these alloys had been used as regular proofs in assaying. This column also

illustrates the higher losses to be expected with increasing amounts of copper, accompanied as they must be by more lead and higher temperatures of cupellation.

TABLE VII—SYNTHETIC ALLOYS

Metals taken	Lead used	Button losses	Cupel absorptions (Mg.)		
GW	Grams	GW	Gold	Silver	Total
All, silver 8					
Gold 980	2.6	12	2.60	0.07	2.67
Copper 10	11	2.34	0.07		2.41
Gold 910	3.2	23	2.35	0.17	2.52
Copper 20		20	2.32	0.10	2.42
Gold 820	3.9	46	4.50	0.09	4.59
Copper 40		45	4.20	0.12	4.32
Gold 700	2.6	8	2.42	0.10	2.52
Copper 5		10	3.03	0.07	3.10
Gold 700	6.5	86	5.87	0.13	6.00
Copper 80		86	6.20	0.23	6.43
Gold 600	2.6	9	2.58	0.14	2.72
Copper 5		11	3.11	0.15	3.46
Gold 500	2.6	10	3.01	0.46	3.47
Copper 5		11	3.19	0.22	3.41
All, silver 10					
Gold 600	3.9	54	4.66	0.30	4.96
Copper 50		57	6.29	0.45	6.74
Gold 500	7.8	98	5.69	0.29	5.98
Copper 90		98	5.91	0.30	6.21
Gold 400	10.4	150	6.17	0.19	6.36
Copper 140		148	5.34	0.26	5.60

The surface of several of the cupels was considerably eaten away and some beads were entrained.

From what has gone before it is evident that while there are not many opportunities for variations in the base-metal assay, these opportunities open the way for very large variations in the result. It is generally assumed that the proof assays will correct for these variations, at least approximately, but if the conditions of the work lead to variations in the assay itself, they must do the same for the proofs, and it is quite possible for the proofs to be very misleading. As a matter of fact, the base-metal proof question is an exceedingly troublesome one to deal with and requires the exercise of much thought and caution.

Substantially the same proof may lead to widely differing corrections when the work is performed under supposedly similar conditions in the same laboratory. Under differing conditions in the same laboratory, and still more so under differing conditions of different laboratories, the proofs may give corrections differing astonishingly. Three samples of standard gold, substantially 900 gold and 100 copper, but with a trifle of silver replacing the copper, were cupelled for base-metal in six laboratories. This would seem to be the simplest and easiest kind of a case, and should show a close agreement among the proofs, but it did not turn out so. One laboratory reported the proof conditions as follows:

BASE PROOFS ON STANDARD GOLD.		ONE LABORATORY
0.0	2.0+	4.2+
0.2+	2.2+	4.5+
0.3+	2.3+	4.8+
0.5+	3.7+	6.8+
0.6+	3.8+	7.2+
0.9+	4.0+	7.3+

The other five laboratories reported the following proofs:

BASE PROOFS STANDARD GOLD Laboratories

1	2	3	4	5
1 charge	2 charge			
1 +	1 5—	5 —	1 +	5 —
2 +	0	1	1 +	5 —
4 +	1 +	0	2 +	3.9 —
5 +	1.5 +	0	2 +	3.9 —
6.5 +	1.5 +	2.8 +	2 +	3.9 —
6.5 +	2 +	2.8 +	2 +	3.3 —
9.5 +				3.3 —
11.5 +				3.5 —
				2.5 —
				1.7 —
				1.7 —

The long row of minus proofs from the fifth laboratory is especially noticeable and indicates too high temperature in the cupelling. The sign + shows that the proof button obtained weighed more than the precious metals going into the proof, while — means that it weighed less. In applying the corrections to the assay buttons the signs must be reversed. These three samples were known to differ slightly in silver and it is scarcely profitable to tabulate the silver results reported.

Another sample of standard gold was sent to five of the above laboratories, several times to each. The laboratory individually quoted above refused to commit itself, as to the copper and silver present, upon its cupellation results. The other four laboratories numbered as above, reported the following proofs:

BASE PROOFS STANDARD GOLD Laboratories			
1	2	3	4
1/2 charge	1/2 charge		
4 —	2 —	1 —	4
3 —	1 —	1 —	3
1 —	0 —	1 —	1
0 —	0 —	0 8—	1
0 7+	1 5 +	0 6—	0
2 +	...	0	3+

These four laboratories reported 58 determinations of silver and base metal, copper, in this sample, summarized as follows:

TABLE VIII—SILVER AND BASE METAL IN STANDARD GOLD							
SILVER		BASE METAL		BASE METAL		BASE METAL	
Fine	Assays	Fine	Assays	Fine	Assays	Fine	Assays
0.25	8	5.0	6	92.0	2	97.0	4
0.50	1	5.5	4	92.5	1	97.5	3
1.0	1	6.0	2	93.0	5	98.0	6
1.5	1	6.5	1	94.0	1	98.5	1
2.0	2	7.0	4	94.5	2	99.0	2
2.5	5	7.5	2	95.0	9	100.0	9
3.0	4	8.0	1	95.5	1		
3.5	4	8.5	1	96.0	11		
4.0	4			96.5	1		
4.5	7		58				

In the above case it was a very simple matter for the assayer to make his proof to correspond very closely in composition to the metal being assayed, but the case of miscellaneous and unknown bullion is often further complicated by the fact that the assayer has to rely on his best judgment in making up his proofs. An experienced assayer can generally form a fairly good estimate for the proof from inspection and the preliminary assay, but small amounts of impurities may be present without being properly adjusted in the proofs, and some of these smaller impurities may have undue influence upon the course of the assay. Again, in a busy commercial laboratory it is often necessary to group closely related bullions under one proof composition which may be a cause of further variations.

In comparing the assays of miscellaneous bullion with the proofs, I wish also to illustrate the influence of the relative position of the cupel in the muffle upon both the proof and the assay. In the following table each horizontal line of figures represents a row of cupels as they stood in the furnace and the figures are the gold weights of the buttons resulting from the cupellations. There is no relation between the rows:

ASSAYS AND PROOFS IN SINGLE ROWS			
Assay	Proof	Assay	Proof
No. 1.....	995.7	997	996.5
No. 2.....	994.6	995	995
No. 3.....	994.1	998	993.4
No. 4.....	633.3	638.3	634.8

COMPOSITION OF PROOFS

	No. 1	No. 2	No. 3	No. 4
Gold.....	605	488	488	268
Silver.....	395	512	512	375
Copper.....	...	...	...	220
Zinc.....	...	...	...	100

The high losses on the proofs in Nos. 1, 2 and 3 are especially noticeable.

In five cases quadruple determinations of base metal were made and were run in two rows of four, one immediately behind the other, with varying arrangement for the assays and proofs. In the table the top row of figures in each set represents the front row of cupels and the figures are the button weights in GW. The assays and proofs are indicated by "A" and "P" respectively.

ASSAYS AND PROOFS IN DOUBLE ROWS			
No. 1.....	A 945.0 P 944.8	P 946.1 A 945.3	P 946.7 P 946.9
No. 2.....	P 996.9 A 994.9	A 997.0 P 996.3	A 995.2 P 996.5
No. 3.....	P 880.8 A 871.0	A 875.8 P 880.8	P 872.1 A 874
No. 4.....	A 961.7 P 961.3	P 962.3 A 960.3	P 963.1 A 962.0
No. 5.....	A 827.8 P 833.0	P 831.7 A 827.0	P 832.1 A 826.3

COMPOSITION OF PROOFS

	No. 1	No. 2	No. 3	No. 4	No. 5
Gold.....	765	865	675	723	590
Silver.....	181	135	210	245	245
Copper.....	54	...	18	32	25
Zinc.....	...	...	100	...	140

In a sixth set the front and back proof differed slightly.

	P 975.8 P 970.8	A 975.4 A 974.2	P 976.0 P 970.0	A 975.3 A 973.8
PROOFS				
	Front		Back	
Gold.....	815		815	
Silver.....	165		160	

Quadruple base-metal assays were made with two sets of samples from two high-grade bullions. Each set of four assays was run by itself with a proof between each pair of assays. The arrangement of figures in the table represents the arrangement of the cupels in the furnace, the top row representing the front row of cupels in each set. The fineness figures represent the combined gold and silver finenesses shown after correcting the button weights by the proof figures in the middle.

TABLE IX—ASSAYS WITH MIDDLE PROOFS, IN DOUBLE ROWS  
1ST BULLION

1ST SAMPLES		2ND SAMPLES			
Gold and silver fineness	Proof	Gold and silver fineness	Proof	Gold and silver fineness	Proof
912.3	2.5 —	912.8	910.4	0.2+	909.3
909.7	1.9 —	911.3	910.5	0.4+	910.3
909.1	2.3 —	908.3	907.5	0.4+	907.1
909.7	2.8 —	909.8	908.6	0	908.3
909.9	2.6 —	911.1	911.8	0.9+	911.5
910.5	3.3 —	912.3	911.5	0.4+	911.5
907.6	3.4 —	913.5	907.7	0.9+	909.0
909.3	2.5 —	909.8	905.9	1.3+	905.4
2ND BULLION					
953.3	1.69—	957.5	964.0	0.5+	952.2
953.2	2.30—	953.0	952.6	0.2—	952.9
954.0	1.37—	953.9	960.8	0.1+	952.6
954.2	2.25—	954.2	958.8	0.4—	959.2
957.7	1.04—	952.2	947.2	3.9+	953.6
955.3	1.75—	953.6	958.0	0.4—	952.2
958.2	1.19—	957.6	957.7	1.8+	957.2
956.6	2.15—	956.3	947.8	2.1+	953.0

COMPOSITION OF BULLIONS AND PROOFS

	Bullions		Proofs	
	No. 1	No. 2	No. 1	No. 2
Gold.....	713.75	758	714	760
Silver.....	198.0	196	200	206
Base.....	88.25	46	Copper	30

These assays were all made in one laboratory by one assayer. The first samples were run at one time and the second at another. A part of the differences shown are undoubtedly due to differences in samples.

This table is worthy of most careful study. It discloses both the remarkable agreement and the utter unreliability of results at times yielded by this method of assay.

Early in the investigation a series of synthetic bullions was prepared for the purpose of elucidating the influence of the composition of the bullion upon the assay results. The samples were distributed to nine laboratories throughout the service and nearly every one was assayed in four laboratories. The results reported, as shown in the next table, indicate that whatever influence the composition may have had on the assaying was masked by other influences in most cases.

TABLE X—BASE AND SILVER IN SYNTHETIC BULLIONS			
BULLION No. 1	BULLION No. 2	BULLION No. 3	BULLION No. 4
Base Silver	Base Silver	Base Silver	Base Silver
4.5 105	1.0 387	1.0 508	1.0 123
8.0 105	3.0 387	1.5 509	1.0 128
9.5 105	4.0 389.5	1.5 509.5	2.5 129.5
9.5 105	5.5 390.5	2.0 509.5	4.0 130
10.0 105.5	6.0 392	2.5 511	5.0 131
10.0 106	...	...	5.0 132
10.5 106	...	...	7.5 134
10.5 107.5	...	...	11.0 134
11.0 111	...	...	8.65
Gold 884.75	Gold 607	Gold 489	
BULLION No. 5	BULLION No. 6	BULLION No. 7	BULLION No. 8
Base Silver	Base Silver	Base Silver	Base Silver
19 356	20.5 160	19.5 443.5	30 239
23 356.5	20.5 161.5	23 447	31.5 240
23.5 358	23 162	23 447	32 241
24 358	23.5 162	23 448	35.5 242
24 358	24 162.5	23.5 448	37 244
24 358	24.5 164.5	24 448	37 244.5
26 359	25.5 165	24 448	37 247.5
26 363	...	28 452	
Gold 618.25	Gold 814	Gold 529	Gold 722
BULLION No. 9	BULLION No. 10	BULLION No. 11	BULLION No. 12
Base Silver	Base Silver	Base Silver	Base Silver
50 181	152 494	161 240	356 362
50 181.5	158 495.5	167 240	359 362
50.5 181.5	159 498	168 240	360 368
50.5 185	159 499	168 240.5	363 368
52 185	159 499	168 242	364 368
52 186	159.5 499	171 242	364 371
54.5 186	161 500	171 243	368 374
55 187	164 501	171 243	370 376
Gold 763.75	Gold 507.5	Gold 590	Gold 268
	Gold 341.5		

Bullion No. 4 contained a small amount of arsenic, about 1 fine, No. 8 contained about the same of antimony. No. 9 was nearly saturated with iron, No. 6 contained both antimony and iron and Nos. 11 and 12 were high in zinc.

Two samples containing arsenic are very interesting. One was approximately 785 fine in gold, 107.5 in silver, 100 in copper and 7.5 in arsenic. The gold assays (65) varied from 779.7 to 792.4, a variation of 12.7 in the fineness. The base assays (24) varied from 101 to 117, a variation of 16 in the fineness. The second was approximately 675 fine in gold, 200 in silver, 100 in zinc, 24 in lead and copper and only 1 in arsenic. The gold assays (62) varied from 671.4 to 681.4, a variation of 10 in the fineness, but the base assays (8) varied less than the gold assays. The base assays varied from 120 to 127, showing a variation of only 7 in the fineness. Evidently both of these bullions are hopeless as assaying propositions.

Two special cases will be mentioned here, although they will also be used further along in this paper. The

Mint service does not pay for silver in deposits when it is less than 8 fine in the bullion. A deposit 884 fine in gold was cupelled 16 times in 5 laboratories for base metal and 12 of the results gave the silver below 8 fine. The 4 at 8 fine and above were all from one laboratory. Also the Service does not buy bullion over 800 fine in base metal, but a synthetic bullion containing about 838 base, most of which was lead, was cupelled for base 16 times in 4 laboratories and 12 of the results ranged from 840 to 836, while a group of four from one laboratory were from 4 to 7 lower in base than the lowest of the 12. The following tables summarize the reports:

BASE METAL AND SILVER IN SPECIAL CASES  
GOLD 884

Base	Assays	Silver
111	1	5
110.25	1	5
110	5	6
109.75	2	6.25
109.50	2	6.50
109	1	7.0
108	1	8.0
107	3	9
	16	

GOLD 110

Base	Assays	Silver
840	2	50
839.5	1	50.5
839	2	51
838.5	1	51.5
838	2	52
837.75	1	52.25
837	1	53
836	2	54
832	1	58
831	1	59
830	1	60
829	1	61
	16	

A few more direct comparisons will be given here, and several others will be found in the sulfocyanate portion of this paper (see September issue).

Various samples of two bullions were assayed for base metal in five laboratories with the following results. Possibly some of the differences shown were due to differences in samples.

1ST BULLION		2ND BULLION	
Assays	Base metal	Assays	Base metal
2	437	1	484
1	438	1	487
1	442	4	488
1	443	1	489
2	444	3	490
1	445	1	492
1	446	1	507
1	448		
1	449	12	
1	453		
14			

A further exceptional illustration is afforded by three bars from each of which two samples were cut and a single assay made on each sample at the purchasing office. These three bars were included in one shipment of redepots. The reposit office remelted the bars and reported much more silver, even after allowing for loss of base metal in remelting. The purchasing office samples were then submitted to two other laboratories in the Service and duplicate assays were made on each sample in each laboratory. The results reported were as follows:

Samples	Bar 1		Bar 2		Bar 3		Bar 4	
	A	B	A	B	A	B	A	B
Original.....	526.25	526	412	412	331	331.5	284.5	284.5
1st Lab.....	539.5	539.5	423.5	423	345.5	344.5	286.5	
2nd Lab.....	537	537	422	424	336	338	286.5	
Gold.....	536	536	421	423	338	336	220.75	
	303.50		265		215			

Having shown that the method is often liable to give erratic results, attention should in justice be directed to the large number of satisfactory agreements shown in Table I. This, also, however, raises a most important physiological and psychological question



which is approached with some hesitation, but the whole object of the investigations upon which this paper is founded is for the purpose of improving our assaying methods as necessarily carried out under commercial conditions, and before this can be intelligently undertaken or successfully accomplished it is essential to consider all the conditions surrounding our present methods and their application. It becomes, therefore, essential to consider the human aspect of the work, since a large laboratory is liable to contain a variety of personalities. Without going into details, three chief factors may be mentioned under this head: pure carelessness, laziness and the domination of one's own or an outside will or intellect. The first one may cause agreement or disagreement, but the second two may surely be counted on to unify the results.

One of the best assayers I have ever known, who was also big and strong enough to be frank, once said to me: "Why I can see any weight at the balance that I want to." The records of the Bureau, particularly the older ones, show far too many cases of remarkable agreement in the reported results to be explained simply upon the general theory of chance.

In one case a sample was sent to an institution on two occasions and assayed in quadruple each time. Everyone of the eight results reported was 0.25 fine in silver. The same sample was sent again and the duplicate results were both given as 4 fine in silver. It was sent again and all four results were stated as 5 fine in silver. In the case of the arsenical bullion already mentioned one laboratory reported the silver at 105, 105, 106 and 107, but on another occasion it was reported by the same laboratory at 106, 109, 110 and 114. In all, 24 determinations of silver were made on this sample in five laboratories and they varied from 101 to 117. Another laboratory shows surprising agreement between duplicates all along the line. A difference of 0.5 in the base-metal duplicates is rare, but when their samples are sent to other institutions for assay, much wider differences are reported, and on one occasion in this laboratory a proof composed of 580 gold, 400 silver and 20 copper lost 20, while a companion proof of the same composition lost only 8. Also a sample of proof gold was once sent to this institution, under the name of fine gold simply, and the report showed 999.5, 999.6, 999.7 and 999.7 fine in gold. Finally in various comparisons the results from this institution form a closely agreeing group of figures at one or the other extreme of all the reports in the comparison. In one instance a docile weigher sitting by the side of a domineering personality turned in many consecutive reports agreeing absolutely with the figures of his associate.

#### CONCLUSIONS REGARDING THE CUPELLATION METHOD

Determinations by difference are always objectionable since all the errors of the other determinations are thrown upon the final one. This allows a wide margin for differences between duplicates and leaves the question of the actual amount of the estimated material present in doubt.

The mass of data here presented warrants the fol-

lowing conclusions regarding the cupellation for base metal: There are two chief sources of operative error in this determination, the absorption of gold and silver by the cupel and the retention of base metal by the precious metal button. At present we do not have the means of controlling either of these with any certainty, or of readily ascertaining their extent in commercial work. These errors may balance each other, but they often fail to do so. A low cupel absorption may be accompanied by either a high or a low button retention, or a high cupel absorption by either kind of button retention, and the relations may be reversed in the duplicates. A third defect arises from the fact that the proofs are subject to the same uncontrollable errors as the assays, and the proof corrections may be fallacious.

Notwithstanding the defects pointed out in this paper, which render the method unsatisfactory, the simplicity and ease of execution of the cupellation method commend its use and undoubtedly it will be extensively employed for many years to come. It is also evident that the defects are inherent and that there is no apparent way of overcoming them in the present state of our knowledge. It, therefore, becomes necessary to seek for a better method, and preferably a direct determination of the silver.

Moreover, aside from the ordinary errors of manipulation, the presence in a bullion of members of the platinum group of metals, which are soluble in nitric acid when alloyed with silver, further complicates the determination of the silver by cupellation. Such bullions are not uncommon in Mint work, although much of the platinum occurs in scrap material purchased.

(To be concluded)

#### THE DETERMINATION OF CHROMIUM AND MANGANESE IN IRON AND STEEL

By FRED C. T. DANIELS

Received May 6, 1914

In steel furnace operations it is frequently necessary to include chromium among elements to be determined in the preliminary analysis. The following 20-minute method has been worked out to fill this necessity. It has been in constant use for the past two years and is sufficiently accurate to be used as a daily routine method, and it occupies but little of the chemist's actual working time.

The method for chromium is an adaptation of the persulfate method for the manganese determination in iron and steel.

The method for manganese is the persulfate method except that the sum of the manganese and chromium is obtained in this titration and the manganese calculated by difference, using the results from the chromium determination. The objection to the usual persulfate method for manganese, in the presence of chromium, is that a varying quantity of the chromium is reduced along with the manganese by the ferrous ammonium sulfate or sodium arsenite. If determined colorimetrically, the chromium gives the solution a different shade, which is difficult to compare. This may be

overcome by using for a standard a steel containing approximately the same amount of chromium as the sample. A still more convenient way is to add the chromium as potassium bichromate, using a standard solution, so that 1 cc. would equal 0.0005 gram of chromium, *i. e.*, 0.25 per cent chromium for a 0.20 gram charge of the sample. This solution is added to the standard after the solutions have been transferred to the color comparison tubes.

**CHROMIUM**—Weigh 1 gram of the sample into a 300 cc. Erlenmeyer flask (Jena glass), add 100 cc. nitric acid (1.135 specific gravity), place on the hot plate, and when solution is complete, boil off all nitrous fumes. (The volume of the solution should not be less than 75 cc. It is unnecessary to filter off the silicon and graphite residue if the solution is complete. When the sample is high in combined carbon, it is well to add a few crystals of ammonium persulfate when the solution is complete and boil a moment longer to destroy the combined carbon.) Remove the flask from the hot plate, add 75 cc. silver nitrate solution (2.00 grams per liter), and immediately 5 grams of ammonium persulfate crystals. Replace flask on the hot plate and bring gently to boiling. Boil vigorously for a minute, and while still boiling add dilute hydrochloric acid, drop by drop, until the permanganate color is completely destroyed. Continue the boiling for one minute and then cool the flask immediately in water. Titrate by adding an excess of tenth-normal ferrous ammonium sulfate solution above that required to reduce the chromium, and titrate back with tenth-normal potassium permanganate solution. The number of cubic centimeters of the ferrous ammonium sulfate oxidized by the chromate, multiplied by 0.00174, gives the weight of chromium in the sample.

**MANGANESE IN THE PRESENCE OF CHROMIUM**—Proceed according to the above directions for the determination of chromium except that after the ammonium persulfate is added, only heat until the solution just comes to boiling, then cool immediately and titrate as before, this time adding enough ferrous ammonium sulfate to reduce both the manganese and chromium. The number of cubic centimeters of ferrous ammonium sulfate used, minus the number used in the chromium determination, multiplied by 0.0055, equals the weight of manganese in the sample.

The ultimate value of the solutions may be used in calculations as above. In this case it is advisable to carry along a blank with a sample containing no chromium and subtracting the blank. The standardization of the solutions against a standard steel is the most satisfactory procedure.

WHEELING MOLD & FOUNDRY CO.  
WHEELING, WEST VIRGINIA\*

## PRINTING INKS AND THEIR ANALYSIS<sup>1</sup>

By J. B. TUTTLE AND W. H. SMITH

Received April 16, 1914

There will be published shortly by the Bureau of Standards, two papers on the subject of printing inks: one, a technologic paper on "The Analysis of Printing

<sup>1</sup> Published by permission of the Director of the Bureau of Standards.

Inks," and the other a circular of general information on this subject. The length of these papers is such as to make it unwise to attempt to present either of them in full at this time, but it is desired to give some idea of their scope.

The first paper treats the subject from an analytical point of view. Four types of ink have been investigated: web press, flat-bed, job, and half-tone inks. These included a number of colored as well as the more common black inks. The method of analysis has been in use for several years for the testing of supplies delivered to the Government Printing Office, and has been found very satisfactory for this purpose.

Using as the solvent a mixture of benzene and ethyl ether, the oil is separated from the pigment by means of a centrifuge. In some cases petroleum ether may be used as the solvent. This method gives an effective separation, and the pigment may be determined with a fair degree of accuracy.

The oil fraction, after evaporating off the solvent, is analyzed for unsaponifiable oils (rosin and mineral oils), rosin, hard gums and linseed oil.

In the black inks, the pigment is ignited and the ash tested for driers and ferric oxide, the latter being the residue left on the ignition of Prussian blue. A qualitative test for Prussian blue is given, which will detect less than one per cent of this material in the pigment. If aniline dyes are present, they may be determined by extraction by means of alcohol, unless preliminary examination shows that the dye is insoluble in this solvent. In the latter event, a suitable solvent must be found.

The colored inks require a preliminary examination to determine the nature of the pigment used, and the method of attack depends largely upon the results of these tests. Some of the mineral pigments, such as vermilion (mercuric sulfide) and chrome green (*i. e.*, the material known commercially as Brunswick or Milori Green), may be determined quantitatively according to the procedure outlined in the original article. If the coloring matter consists of aniline dyes or lakes, it will usually be found sufficient to determine whether or not these colors are fast to light. Two methods for this test are given.

A table is given showing how closely one may expect duplicate determinations on the same sample to check. These figures are the result of testing several hundred samples of ink by at least half a dozen analysts, so that they may reasonably be taken as a fair measure of the accuracy of the method.

The paper also includes a brief discussion of the relation of these laboratory tests to the practical tests which may be made by the printer. It is not the intention that the latter shall be supplanted by the former, but that the two shall supplement each other in order to obtain the grade of ink which is the most suitable for the purpose.

The second paper is the circular of information on the general subject of printing inks. It gives a brief description of some of the materials used in the manufacture of ink, and also treats broadly some of the problems concerning the relation between the ink

and the paper. While the first paper will probably be of more particular interest to chemists, this circular, it is hoped, will appeal to all those who may desire some general information on the subject. It will include at first, only the same classes of ink covered by the technologic paper, but it is proposed to revise this circular from time to time, adding to it other classes of ink as rapidly as accurate and reliable information about them can be obtained.

Anyone who is interested in the subject of printing inks, may obtain either one, or both of these publications, on application to the Bureau of Standards, Washington, D. C.

BUREAU OF STANDARDS, WASHINGTON

## THE OCCURRENCE OF MANGANESE IN KENTUCKY SOILS AND ITS POSSIBLE SIGNIFICANCE

By O. M. SHEDD

Received April 22, 1914

### HISTORICAL

Although manganese is not generally regarded as one of the essential elements of plant food, nevertheless numerous experiments have shown that its compounds are invariably present in soils and in a large variety of plants and animals which necessarily derive their sustenance from the soil. The fact having been generally proven that it is universally present in plants has caused considerable work and discussion as to what function it performs and whether or not the application of some manganese salts will prove beneficial to plant growth.

In the analysis of 23 Italian soils of various kinds (sandy, volcanic, clay and calcareous), Contino<sup>1</sup> found that manganese was always present in amounts varying from a trace to as much as 0.48 per cent  $Mn_2O_4$ , the average being 0.17 per cent  $Mn_2O_4$ .

De Sornay<sup>2</sup> has shown in the analyses of 37 Mauritius soils that the manganese varies from 0.03 to 0.41 per cent, the average being from 0.15 to 0.20 per cent. He also found that some plants contain considerable manganese in their ash, the proportion in the natural plants being usually less than 0.01 per cent but is universally present indicating that plants assimilate it naturally. These results have been confirmed by Boname<sup>3</sup> who found as much as 1.26 per cent of manganese in arrowroot grown in Mauritius soils.

In this country, Sullivan and Robinson<sup>4</sup> have found that of 26 American soils recently analyzed, all contain manganese ( $MnO$ ) in proportions ranging from 0.01 to 0.51 per cent. The average content is 0.20 per cent, or about 8000 pounds per acre foot.

Gortner and Rost<sup>5</sup> have found in a few Nebraska soils that the average manganese content is about 0.11 per cent  $MnO$ .

Jadin and Astruc<sup>6</sup> give the results of analyses of about 65 species of plants in which it is shown that this

element is widely distributed in the plant kingdom. The amount present was found to vary with the different organs of the plant examined. The manganese content of different plants belonging to the same family could not be taken as indicative of the average content to be expected in other members of the order. The chlorophyll portions were, as a rule, richer in this element than the subterranean parts and the percentage was greater in the older leaves, especially when the fresh weight is taken, but often the reverse if the ash weight is considered.

McHargue<sup>1</sup> has determined the manganese in a variety of plants and his results confirm those of Jadin, Astruc and others who might be mentioned, that this element varies considerably in the different organs of the same plant and of course in different plants.

Furthermore, Bertrand and Medigreceneau<sup>2</sup> have found traces of this element in about 60 species of wild and domestic animals and it is therefore thought that its presence has some physiological significance and is not merely accidental as is commonly supposed.

Experience has shown that the presence of excessive manganese compounds in the soil are very injurious to vegetation as they act directly on the chlorophyll and cause bleaching or yellowing of the leaves. For instance, Kelley<sup>3</sup> has found, in Hawaii, that certain black lands on which pineapples did not grow well, showed the presence of from 2.43 to 9.74 per cent  $Mn_2O_4$  and indicated a close relation between the manganese content of the soils and the general appearance and growth of the pineapples. Other areas in close proximity in which they thrived, contained considerably less manganese; otherwise the soils were the same. Moreover, it was found that when an attempt was made to grow other plants in these soils, there invariably occurred a yellowing of the leaves and premature falling of the lower ones. His conclusions were that soils that contain over 4 per cent of manganese are not suitable for the growth of pineapples.

Guthrie and Cohen<sup>4</sup> also found that bare patches of grass soil showed 0.254 per cent  $Mn_2O_3$ , while other portions of the soil in which the grass was growing well, contained much less. No other differences were found. They suggest that the element was present originally in innocuous form which became toxic by oxidation. It is interesting to note in both cases that the application of soluble phosphates had a tendency to correct these toxic conditions and in the case of the grass, restored its growth.

Ewell<sup>5</sup> gives another illustration in reporting the results of an examination of a soil which failed to grow legumes and which was found to contain considerable amounts of manganese compounds soluble in water, more in fact than of lime.

It has been claimed that manganese serves no useful purpose in plants but that it is merely taken from the

<sup>1</sup> *Stat. Spec. Agar. Ital.*, **44** (1911), 51-55; *J. Chem. Soc.* (London), **1911**, Aii, p. 649.

<sup>2</sup> *J. Chem. Soc. (London)*, **1912**, Aii, p. 1089.

<sup>3</sup> *Exper. Sta. Rec.*, **21** (1909), 717.

<sup>4</sup> *U. S. D. A., Bur. Soils, Circ.* **75**, p. 3; *Exper. Sta. Rec.*, **28** (1913), 523.

<sup>5</sup> *THIS JOURNAL*, **4** (1912), 522.

<sup>6</sup> *Compt. rend. Acad. Sci. (Paris)*, **156** (1913), 26, 2023-24; *Exper. Sta. Rec.*, **29** (1913), 28, 628.

<sup>1</sup> *Ky. Agr. Exper. Sta.*

<sup>2</sup> *Compt. rend. Acad. Sci. (Paris)*, **154** (1912), 15, 941-3; **22**, 1450-52; *Exper. Sta. Rec.*, **27** (1912), 670.

<sup>3</sup> *Hawaii Sta., Press Bull.* **23**, 14; *Rept.*, **1909**, pp. 58-63; **1910**, pp. 14-16, 41-43, 45-50.

<sup>4</sup> *Agr. Gaz. N. S. Wales*, **1910**, 21, 219-222; **1911**, 22, 1, 70; *J. Chem. Soc. (London)*, **1910**, Aii, 444; *Exper. Sta. Rec.*, **25**, 122.

<sup>5</sup> *Science*, N. Ser., **16** (1912), 339, 291; *Exper. Sta. Rec.*, **14**, 231.



soil as are some other non-essential elements, and from plants finds its way into the animal organism. This view has led a number of investigators to conduct experiments to determine if manganese compounds would have any practical use in agriculture and the opinion of the majority is that under certain conditions they may have a decided value.

From their work with water, sand and soil cultures, Salomone,<sup>1</sup> Stoklasa,<sup>2</sup> Leidreiter,<sup>3</sup> Katayama,<sup>4</sup> Loew<sup>5</sup> and Aso<sup>6</sup> have come to the conclusion that small amounts of manganese are decidedly beneficial to some plants, while large amounts are toxic. In these experiments, the manganese salts used included the phosphate, carbonate, nitrate, sulfate and others and were tried on a variety of plants such as oats, wheat, potatoes, sugar beets, rice and a large number of vegetables.

In pot and field experiments on different crops, using manganese salts, very favorable results have been obtained provided the right quantities are used, but here as in the above trials, it has again been demonstrated that large quantities are injurious.

Bertrand<sup>7</sup> has made experiments on a clay soil containing 0.057 per cent of manganese soluble in hydrochloric acid and 0.02 per cent soluble in boiling acetic acid. Oats were grown on 2 plots of 20 acres, both of which had the usual manures and one pure manganese sulfate at the rate of 44 pounds per acre. The manganese salt resulted in a gain of 17 per cent of grain and 26 per cent of straw. The grain from both plots contained the same amount of the element.

In plot tests with grain, using different manganese compounds, Stranipelli<sup>8</sup> obtained increased yields due to their effect, the greatest increase resulting from the use of the sulfate.

Ray and Pradier<sup>9</sup> have found that the use of manganese sulfate on apricots produced a more luxuriant vegetation and increased the size of the fruits.

Stoklasa<sup>10</sup> increased the yield of sugar beets from 30 to 50 per cent by adding about 8 pounds of manganese and 4 pounds of aluminum per acre, in the form of sulfates, to a complete basal fertilizer. The assimilable aluminum salt apparently corrected the toxic action and promoted the stimulating effect of the manganese.

Very good results have been obtained by Boullanger<sup>11</sup> with manganese fertilizers on potatoes, oats, peas, clover and some truck crops.

Extending its use somewhat further, Sanning and Tosatti<sup>12</sup> report results indicating that manganese sulfate tends to increase the yield of grapes considerably

while McCallum<sup>1</sup> has obtained remarkable results in the growth of potatoes by preliminary treatment of the tubers with manganese chloride. Seed potatoes thus treated, while showing no difference in the growth of foliage, exhibited a most pronounced acceleration in the formation of tubers.

Loew and others referred to above, who are connected with the Tokyo Imperial University, have for a number of years made numerous experiments in Japan on the effect of manganese salts on various crops. They have obtained some very favorable and interesting results, especially with rice.

Others might be mentioned who have experimented with manganese fertilizers and while the results of some are indifferent or negative, still those of the majority are favorable. This of course is to be expected in work of this character, which, being only in its experimental stage, involves many unknown factors such as the amount and kind of material used, the character and location of the soil and the crop grown on it.

While the experiments have covered a wide field and included a large number of investigators, it is interesting to note that identical conclusions regarding the use and function of manganese compounds in plants have been independently agreed upon by several of the workers. Briefly stated, these conclusions are as follows:

1—Small applications of manganese compounds are in many cases beneficial, while large applications are invariably toxic.

2—The presence of manganese plays a very important part in the formation of chlorophyll in the leaf and hence performs an important function in carbon assimilation by promoting rapid photosynthesis in the chlorophyll apparatus.

3—When small amounts of manganese compounds occur in natural soils, it is believed that a two-fold function in plant growth is performed. One is that they act catalytically, increasing the oxidation in the soil and accelerating auto-oxidation in plants, and furthermore, they tend to modify the absorption of lime and magnesia by partially replacing them from insoluble combinations and to exert a direct effect on the osmotic absorption of both.

4—That manganese is invariably associated with the oxidases in plants and stimulates their action has been proven by Bertrand and others, while Loew considers it probable that very fertile soils are characterized by the presence of readily available compounds of this element.

#### EXPERIMENTAL

As a considerable number of carefully selected soils had been used by the writer in some former work in comparing the amount of total sulfur in continuously cultivated soils and subsoils with the corresponding virgin samples, it was thought that it might prove of interest to use these for total manganese determinations, in order to find out what effect continuous cultivation might have on this element. A description of the locality where the samples were taken, the ro-

<sup>1</sup> *Chem. Zentr.*, 1906, ii, 532; *J. Chem. Soc.*, (London) 1906, Aii, 792.

<sup>2</sup> *Compt. rend.*, 1892 (1911), 1340-42; *J. Chem. Soc.* (London), 1911, Aii, 643.

<sup>3</sup> *Bied. Zentr.*, 40 (1911), 531-35; *J. Chem. Soc.*, 1911, Aii, 923.

<sup>4</sup> *Bull. Coll. Agr. Tokyo Imp. Univ.*, 7 (1906), 91-93.

<sup>5</sup> *Ibid.*, 5 (1902), 161-172.

<sup>6</sup> *Ibid.*, 5 (1902), 177-185.

<sup>7</sup> *Compt. rend. Acad. Sci. (Paris)*, 141 (1905), 26, 1255-57; *Exper. Sta. Rec.*, 17, 954.

<sup>8</sup> *Atti. 6 Cong. Inter Chem. Appl.*, 4 (1906), 14 17.

<sup>9</sup> *Exper. Sta. Rec.*, 22 (1910), 718.

<sup>10</sup> *Ibid.*, 26 (1912), 225.

<sup>11</sup> *Ibid.*, 29 (1913), 838.

<sup>12</sup> *Ibid.*, 29 (1913), 838.

<sup>1</sup> *Aris. Sta. Rept.*, 1909, pp. 584-86.

tation and number of years of cultivation, together with the yields of crops usually produced on the old and new land were given in a former publication.<sup>1</sup> It is not necessary to repeat these data here, except it might be stated that in a large majority of instances the soils had been continuously cultivated for a considerable number of years and no stable manure or commercial fertilizer had been used.

The procedure used for the determination of total manganese was practically the same as that employed by Gortner and Rost in their work referred to above and consisted of what is commonly known as the sodium bismuthate method. They have shown that their method which consists in fusing the soil with sodium carbonate to obtain the manganese in solution and its subsequent oxidation to permanganic acid with sodium bismuthate gives higher and more concordant results on Nebraska soils than Walters' method in which ammonium persulfate is employed as the oxidizing agent. The Walters method<sup>2</sup> had, until this time, been regarded as the most accurate method, either gravimetric or volumetric, known for this purpose and was adopted by Hillebrand<sup>3</sup> and Washington<sup>4</sup> for the determination of total manganese in rocks.

It is only necessary to examine the results obtained by Gortner and Rost to be convinced that their method is simpler and more accurate than that of Walters; in fact Blair<sup>5</sup> and Brinton<sup>6</sup> have recognized the superiority of the sodium bismuthate oxidation by stating that "for samples containing not over 2 per cent of manganese, the bismuthate is the most accurate method known."

The method as used in this work is as follows: One gram of soil is intimately mixed with 4 grams of manganese-free, dry, sodium carbonate and fused in a 20 cc. platinum crucible over a blast lamp until the melt is quiet or for about ten minutes. The liquid mass is then poured into a 100 cc. platinum dish and the dish rotated in order to obtain the melt in a thin film, thus providing for more rapid solution. The melt and crucible are then treated with about 100 cc. of distilled water and heated on the water bath until the fused product is completely disintegrated, which requires about an hour or two. The crucible is then removed from the dish, any adhering solution washed off, and the mixture acidified with 130 cc. of 35 per cent (by weight) sulfuric acid and diluted to 250 cc. Should there be a heavy precipitate of silica at this point it is advisable to filter, using a Buchner funnel and filtering by suction. This is seldom necessary, however, for in most cases the silica does not precipitate to any extent, but merely produces a slight opalescence which does not interfere with the permanganate readings. One hundred cc. of this solution are then placed in an Erlenmeyer flask, the contents brought to boiling, cooled, and 0.50 gram Baker's C. P. sodium bismuthate

added. The amount of bismuthate to be added, of course, depends on the quantity of manganese present and might vary from 0.25 gram to 1 gram. It is advisable not to add any large excess so that the bismuth salts will remain in solution. It has been found that 0.25 gram of bismuthate is sufficient where the manganese content does not exceed 0.20 per cent. The oxidation mixture is then heated just to boiling and continued only until the liquid has the true permanganate color, which requires only a minute or two. The solution at this point may have a slight foreign red color but this will disappear on cooling. Excessive heating of the solution is to be avoided as this tends to destroy the permanganate color and gives low results. After cooling, the solution is made to its original volume, or 100 cc., shaken thoroughly and if any bismuthate salts precipitate, it is allowed to stand for some minutes in the dark until these settle. If it is found necessary in order to obtain a clear solution, it can be filtered through properly prepared asbestos, but as soon as possible the solution is read in a colorimeter or Nessler's glasses against a standard solution of permanganic acid which has been prepared by reducing a solution of potassium permanganate in 20 per cent (by weight) sulfuric acid by the cautious addition of sulfurous acid, and reoxidizing with bismuthate. The standard solution should contain about 0.2 mg. of MnO per 10 cc. From the ratios thus obtained, the quantity of manganese in the original sample is calculated.

The writer in this work used a Duboscq colorimeter and the standard was prepared as described above and compared every day with a freshly prepared potassium permanganate solution, 10 cc. of which = 0.2 mg. MnO. The standard permanganic acid solution was found to deteriorate gradually in strength and as a potassium permanganate solution of the same manganese strength was found to have the same color, a factor could be used on the true standard. The potassium permanganate standard could just as well be used as a standard but as it was thought best to have both the standard and unknown solution prepared in the same manner, the permanganic acid standard was employed throughout the work.

It might also be mentioned here that a potassium permanganate solution of this weak strength gradually deteriorates, so the plan followed was to make the permanganate solution daily, by the proper dilution of a N/10 solution, and the permanganic acid standard, every four or five days. In both, boiled distilled water was used to which a few drops of weak permanganate were added until just faintly colored.

Gortner and Rost used the permanganate reduced with sulfurous acid as a stock solution which they found to be stable and from which they made their standard as needed, but the writer prefers the other plan since the exact strength of the standard can be determined with very little trouble.

The method has given very good duplicate results on independent fusions while it might be mentioned that blank determinations showed no manganese present in the chemicals used.

<sup>1</sup> *Ky. Agr. Exper. Sta. Bull.*, **174**.

*Chem. News*, **83** (1901), 76; **84** (1901), 239.

*Bull.*, **422**, 116, U. S. Geol. Survey.

<sup>2</sup> "The Chemical Analysis of Rocks," Wiley & Sons, N. Y., 1910.

<sup>3</sup> "Chemical Analysis of Iron," 7th ed., p. 121, J. Amer. Chem. Soc.,

26, 793.

<sup>6</sup> *This Journal*, **3** (1911), 237.

In the following tables, the samples in which the results are strictly comparable, both in the surface and subsoil of the virgin and cultivated areas, are given

TABLE I—TOTAL MANGANESE IN KENTUCKY SOILS RESULTS IN PERCENTAGES AND POUNDS PER ACRE

No.	COUNTY	EASTERN COAL FIELDS AREA			SURFACE SOIL			SUBSOIL		
		Virgin	Cultivated	%	Virgin	Cultivated	%	Virgin	Cultivated	%
669-72.....	Wolfe	0.152	0.3040	0.072	1440	0.122	2440	0.054	1080	
700-1.....	Magothin	..	..	0.077	1540	..	..	0.051	1020	
702-3.....	Johnson	..	..	0.050	1000	..	..	0.031	620	
704-5.....	Johnson	..	..	0.068	1360	..	..	0.076	1520	
763-4.....	Johnson	0.050	1000	..	..	0.009	180	..	..	
706.....	Floyd	0.148	2960	..	..	..	..	..	..	
707-10.....	Perry	0.078	1560	0.067	1340	0.063	1260	0.036	720	
715-18.....	Lawrence	0.060	1200	0.027	540	0.037	740	0.009	180	
731-4.....	Pike	0.125	2500	0.078	1560	0.095	1900	0.063	1260	
AVERAGE.....		0.102	2043	0.063	1254	0.065	1304	0.046	914	
ST. LOUIS-CHESTER AREA										
681-2.....	Lyon	..	..	0.026	520	..	..	0.022	440	
683-4.....	Metcalfe	..	..	0.050	1000	..	..	0.018	360	
685.....	Adair	0.101	2020	..	..	..	..	..	..	
759-60.....	Lincoln	0.134	2680	..	..	..	..	..	..	
806-9.....	Warren	0.065	1300	0.033	660	0.063	1260	0.031	620	
814-4.....	Metcalfe	In first 18 inches	..	..	0.192	3840	0.089	1780	..	
815-6.....	Metcalfe	In first 18 inches	..	..	0.080	1600	0.094	1880	..	
AVERAGE.....		0.100	2000	0.036	727	0.063	1260	0.024	473	
CINCINNATIAN AREA										
757-8.....	Henry	0.094	1880	0.053	1060	..	..	..	..	
769-70(a).....	Washington	0.320	6400	0.159	3180	..	..	..	..	
771.....	Washington	..	..	0.204	4080	..	..	..	..	
772.....	Washington	..	..	0.136	2720	..	..	..	..	
773(b).....	Mason	..	..	0.215	4300	..	..	..	..	
775(b).....	Mason	..	..	0.215	4300	..	..	..	..	
774(b).....	Mason	..	..	0.248	4960	..	..	..	..	
AVERAGE.....		0.207	4140	0.176	3514	..	..	..	..	
WESTERN COAL FIELDS AREA										
692-5.....	Webster	0.027	540	0.017	340	0.024	480	0.015	300	
821-4.....	Henderson	0.099	1980	0.076	1520	0.036	720	0.031	620	
841-4.....	Muhlenberg	0.308	6160	0.205	4100	0.116	2320	0.062	1240	
AVERAGE.....		0.145	2893	0.099	1987	0.059	1173	0.036	720	
KOOKUK-WAVERLY AREA										
686.....	Adair	..	..	0.031	620	..	..	..	..	
723-6.....	Adair	0.005	100	0.019	380	0.002	40	0.015	300	
688-91.....	Rockcastle	0.011	220	0.029	580	0.010	200	0.012	240	
696-9.....	Green	0.177	3540	0.166	3320	0.132	2640	0.115	2300	
AVERAGE.....		0.064	1287	0.061	1225	0.048	960	0.047	947	
QUATERNARY AREA										
719-22.....	Graves	0.246	4920	0.216	4320	0.072	1440	0.024	480	
845-8.....	Cracken	0.148	2960	0.225	4500	0.046	920	0.091	1820	
AVERAGE.....		0.197	3940	0.221	4410	0.059	1180	0.058	1150	
TRENTON AREA										
749-3.....	Clark	0.258	5160	0.182	3640	0.264	5280	0.160	3200	
750-4.....	Clark	..	..	0.245	4900	..	..	0.198	3960	
751-2.....	Clark(c)	0.228	4560	0.215	4300	..	..	..	..	
755-6.....	Fayette	0.273	5460	0.225	4500	0.254	5080	0.225	4500	
765-8.....	Woodford	0.252	5040	0.227	4540	0.227	4540	0.139	2780	
783-40.....	Madison	..	..	..	..	..	..	..	..	
AVERAGE.....		0.253	5055	0.219	4376	0.248	4967	0.181	3610	
DEVONIAN AREA										
727-8.....	Clark	0.147	2940	0.142	2840	..	..	..	..	
764-2.....	Marion	0.047	940	0.018	360	0.015	300	..	..	
833-6.....	Madison	0.012	240	0.007	140	0.003	60	0.002	40	
AVERAGE.....		0.069	1373	0.071	1427	0.003	60	0.002	40	
SILURIAN AREA										
817-20.....	Jefferson	0.166	3320	0.194	3880	0.107	2140	0.136	2720	
829-32.....	Madison	0.022	440	0.022	440	0.018	360	0.015	300	
AVERAGE.....		0.094	1880	0.108	2160	0.063	1250	0.076	1510	
RIVER ALLUVIAL AREA										
676-7.....	Daviess	0.218	4360	0.163	3260	..	..	..	..	
678-80.....	Daviess	0.166	3320	0.131	2620	..	..	..	..	
679.....	Daviess(d)	..	..	0.031	620	..	..	..	..	
711-14.....	Jefferson	0.331	6620	0.215	4300	0.163	3260	0.105	2100	
825-8.....	Henderson	0.038	760	0.038	760	0.032	640	0.022	440	
AVERAGE.....		0.188	3765	0.137	2735	0.098	1950	0.064	1270	

(a) Nos. 769 to 772 were taken on the same farm but Nos. 771 and 772 had been cultivated for a longer time.

(b) All on the same farm but the number of years that each had been in cultivation was as follows: No. 773, 62 years; No. 775, 33 years; and No. 774, 9 years.

(c) Taken from the same field as the one just above it. In this particular area the tobacco was a failure while in the remainder of the field it was growing well. No material differences in the chief plant food elements which might account for it were found from a chemical analysis.

(d) Omitted from the average. This soil is of a peaty character and the river overflows it three or four times a year.

in the same horizontal line. In computing the percentages of manganese to pounds per acre, the calculations were made by assuming the surface, or first 6 1/2 to 7 inches of soil as weighing 2,000,000 pounds, and the second 6 inches or subsoil, as weighing the same. The pounds per acre of manganese given for the subsoils approximately represent the second 6 inches, or from 6 1/2 to 12 1/2 inches, although the subsoil samples were usually taken from 6 to 18 inches in depth. This of course assumes that the second and third 6 inches of soil will have about the same manganese content and they probably will be close enough so that the differences which are shown in the tables between the surface soils and subsoils, taken to these depths, will not be materially changed.

The soils, with the amount of manganese reported as the element, have been arranged according to the geological areas to which they belong and all the areas found in this state are more or less represented in Tables I and II.

TABLE II—AVERAGE NUMBER OF POUNDS PER ACRE OF MANGANESE IN THE GEOLOGICAL AREAS OF KENTUCKY AND PERCENTAGE LOSS DUE TO CULTIVATION

AREA	SURFACE			SUBSOIL		
	Virgin	Cult.	Loss %	Virgin	Cult.	Loss %
Eastern coal fields.....	2043	1254	39	1304	914	30
St. Louis-Chester.....	2000	727	64	1260	473	62
Cincinnati.....	4140	3514	15	1173	720	39
Western coal fields.....	2893	1987	31	960	947	1
Kookuk-Waverly.....	1287	1225	5	1180	1150	3
Quaternary.....	3940	4410	12(a)	4967	3610	27
Trenton.....	5055	4376	13	60	40	33
Devonian.....	1373	1427	4(a)	1250	150	21(a)
Silurian.....	1880	2160	15(a)	1950	1270	35
Average.....	3765	2735	27	1950	1270	35

(a) Increase.

## DISCUSSION

The various amounts of manganese found in the different samples disclose some very interesting facts when the known fertility of the areas is considered, the chief of which is that the best agricultural areas contain the largest amounts of this element, as they do of some of the essential elements of plant food.

The geological areas in Tables I and II are arranged according to their size, the Eastern Coal Field occupying the greatest territory. If a comparison now be made of the areas containing from the largest to the smallest number of pounds per acre of sulfur and phosphorus found in these soils, in the earlier work, with the amount of manganese, there is seen to be an interesting relation existing between these three elements. To illustrate this Table III is given, the areas in which are abbreviated, and commencing at the top of the column, under each element, the area is first given which was found to have the largest number of pounds per acre of that element and so on down the column for the other areas in regular order according to the diminishing amounts found. In this connection it might be mentioned that of the three elements, sulfur was usually found in the smallest and manganese in the largest amounts in these soils.

From the standpoint of the store of fertility in the soils of the different areas and their agricultural value, the Trenton undoubtedly occupies first place and the Cincinnati second. The approximate order of importance of the remainder might be classified as follows: River Alluvial, Devonian, St. Louis-Chester, Silurian,



TABLE III—RELATION EXISTING BETWEEN THE SULFUR, PHOSPHORUS AND MANGANESE IN THE GEOLOGICAL AREAS OF KENTUCKY

VIRGIN SURFACE			CULTIVATED SURFACE			VIRGIN SUBSOIL			CULTIVATED SUBSOIL		
Sulfur	Phosphorus	Manganese	Sulfur	Phosphorus	Manganese	Sulfur	Phosphorus	Manganese	Sulfur	Phosphorus	Manganese
D	T	T	T	C	Q	St L-C	T	T	St L-C	T	T
C	D	C	R A	C	Q	R A	R A	R A	R A	R A	R A
T	C	Q	C	D	C	T	E C F	E C F	St L-C	E C F	St L-C
R A	R A	R A	C	R A	R A	E C F	W C F	W C F	S	W C F	W C F
E C F	E C F	W C F	W C F	E C F	W C F	W C F	Q	Q	E C F	E C F	E C F
W C F	Q	St L-C	S	S	S	W C F	St L-C	W C F	W C F	W C F	W C F
Q	W C F	S	E C F	W C F	E C F	Q	D	K-W	K-W	K-W	St L-C
St L-C	St L-C	D	K-W	K-W	K-W	K-W	D	D	Q	Q	D
K-W	K-W	K-W	Q	St L-C	St L-C						

Quaternary, Eastern and Western Coal Fields and finally the Keokuk-Waverly, which is generally regarded as the poorest of all.

In a majority of the samples, the cultivated surface as well as the subsoils show considerable losses of manganese when compared with the corresponding virgin. Furthermore, the surface soils of both generally contain more of this element than their respective subsoils.

The counties in which the soils were collected for this work were Wolfe, Graves, Warren, Henderson and Madison; also Nos. 813 to 820 from Metcalfe and Jefferson, or a total of forty samples. The above holds true in all with respect to the manganese content of the surface compared with its subsoil, while in three instances the virgin surface contained less and in two the same amounts of manganese as the cultivated samples.

The remainder of the samples were generally selected from those sent in by the residents of the state for chemical analysis and as it is sometimes difficult to obtain the accurate history of a field for several years past, since in certain sections much of the land is rented to tenants, it would have been better to collect all for this work, but this would have caused considerable delay.

In the Keokuk-Waverly area, commercial fertilizers were used while in some of the others it is very probable that commercial fertilizers or manure had been used in former years. This may partly account for the fact that the manganese content has been maintained in the soils of this area as well as in some of the others.

The large losses of manganese in some of the cultivated soils are hardly to be explained as due to the amounts removed by the different crops grown on them for the accumulated analyses show that the ordinary crops do not contain sufficient amounts of this element to justify this conclusion. It may be that cultivation converts the manganese compounds into soluble forms which are readily leached out and thus lost in the drainage water. This is a matter that needs further investigation, and the writer desires, as soon as an opportunity affords, to examine some of the surface and deeper drainage waters of the different areas in order to determine to what extent this element is present.

#### SUMMARY

I—It has been proven by different observers that manganese is universally present in soils, plants and many animals.

II—The majority of the experiments show that the application of certain manganese compounds, particularly the sulfate, to some crops, is decidedly beneficial. These experiments have further shown that while small applications are in many cases beneficial to plants, large applications are generally harmful.

III—In a large majority of the soils examined, the writer found considerably less manganese in the cultivated surface than in the corresponding virgin samples. The same holds true for the subsoils.

IV—In practically every case, the surface soils of the virgin and cultivated areas contain larger amounts of this element than their respective subsoils.

V—When some former work on these samples is considered, it is found that a majority of the soils contain considerably more manganese than phosphorus, but many samples have much less, while the losses of manganese in the cultivated areas are usually greater than of phosphorus.

VI—There are large differences in the manganese content of the soils of the different geological areas and sometimes in those from the same area. The amounts found in the surface soils vary from 0.005 to 0.331 per cent, and in the subsoils from 0.002 to 0.264 per cent.

VII—As a rule, the better agricultural areas contain much larger amounts of manganese than the inferior areas.

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#### ON THE COMPOSITION AND VALUE OF BAT GUANO

By C. F. MILLER

Received April 20, 1914

At various points in this country, especially in the warmer regions, caves exist which are frequented by bats in such numbers that their excrement or "bat guano" has accumulated in amounts sufficient to give it some commercial importance as a fertilizer.

Generally, the amount of guano is rather limited in any one deposit and in the aggregate, the entire quantity now in sight, or probably to be discovered in this country, is not sufficient to appreciably affect the fertilizer industry. On the other hand, such a deposit may represent a considerable fortune to the individual discoverer or owner, and the frequency with which these small deposits occur, justifies a short discussion of their composition and value.

The following table containing the results of analyses of bat guano samples sent to this Bureau from time to time, shows their composition as well as the locality from which they were taken.

BAT GUANO ANALYSES				
Results in percentages, based on air-dry sample				
LOCATION	N(a)	P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O	ANALYST
Near Carlsbad, N. M.	4.24	2.31	1.28	J. A. Cullen
Gundeloupe Mts., N. M.	1.77	2.68	0.41	40.0 C. F. Miller
Torreon, N. M.	10.82	1.08	1.01	W. H. Waggaman
Oregon Co., Mo.	8.10	2.06	0.58	B. E. Brown
San Juan, Porto Rico(b)	1.00	3.40	0.21	W. H. Waggaman
San Juan, Porto Rico(b)	0.50	2.40	0.29	W. H. Waggaman
El Fondo, Santo Domingo, Haiti	11.84	4.80	1.61	90.0 C. F. Miller

(a) Determined by Mr. T. C. Treseott, of the Bureau of Chemistry.

(b) Both of these samples contained considerable calcium carbonate.

Both potash ( $K_2O$ ) and phosphoric acid ( $P_2O_5$ ) were determined by the official method for fertilizers, the former by treatment with concentrated sulfuric acid, ignition and extraction with dilute hydrochloric acid; the latter by treatment with a solution of magnesium nitrate, evaporation, ignition and a similar extraction.

A glance at the table shows that a wide variation exists, not only in the percentages of the fertilizer constituents present, but also in the ratios of nitrogen to phosphoric acid, nitrogen to potash or phosphoric acid to potash. This large variation is attributable to either one, or both of two things: (1) The presence of considerable extraneous matter such as rock débris, etc., or (2) the removal of some of the more available constituents by leaching, or, in the case of nitrogen, by decomposition of the material and subsequent volatilization as ammonia.

It may be said in this connection, that in the more recent deposits, nitrogen is the most valuable constituent, phosphoric acid and potash following in the order given; but on "aging," the nitrogen content decreases very rapidly since most of it is present in an available form.<sup>1</sup>

The writer wishes to place particular stress on the sample from Haiti as it represents uncontaminated and practically undecomposed bat guano which is very likely of recent origin, since thousands of bats<sup>2</sup> spend their days in the cave at the present time. As received in the laboratory, it consists of a dry, dark brown powder, in which the wings and other parts of insects can be seen by the naked eye.<sup>3</sup>

Over 90 per cent of the phosphoric acid present is water-soluble as is also the greater part of the potash; and if the high percentage of nitrogen, together with the large amount of organic matter (as shown by the volatile determination), are reckoned with these facts, it is evident that the substance is very valuable.

It has been calculated from data concerning the Haitian cave (which had not been fully explored at the time) that it contains approximately seven hundred tons of bat guano. Based on the market prices of 20 cents per pound for nitrogen,<sup>4</sup> and 5 cents per pound for phosphoric acid and potash, the material is worth (not considering the organic matter, which is a big factor) very close to \$40 per ton, or approximately \$30,000 for the entire deposit. Whether or not this is a representative example is a matter for conjecture, but very likely it is above the average in quantity and it certainly is in quality.

No specific data on the extent of the American deposits already discovered, are available. In several instances, however, they were reported as being of considerable size.

The facts given in this paper warrant the suggestion that a further search for bat guano be made, since

there is a possibility, or even a probability, of the existence of other valuable, and as yet undiscovered deposits in this country.

BUREAU OF SOILS  
U. S. DEPARTMENT OF AGRICULTURE  
WASHINGTON

## STUDIES IN SYNTHETIC DRUG ANALYSIS—I. ESTIMATION OF ACETANILIDE AND PHENACETIN IN ADMIXTURE

By W. O. EMERY<sup>1</sup>

Received April 30, 1914

### INTRODUCTION

During the past few years, more particularly since the inception of both federal and State drug enactments, attention has been directed repeatedly to the dearth of adequately tested methods for detecting and estimating medicinal agents. The need of these methods was most keenly felt in connection with certain inhibited substances of synthetic character like acetanilide and its derivatives, antipyrin, cocaine, codeine, heroin and other similarly potent drugs, which find extended application in many of our proprietary medicines.

Aside from these considerations, however, there existed in the case of acetanilide and phenacetin (acetphenetidin) additional cause, on the part of drug analysts at least, for desiring quantitative methods. The relatively low cost of acetanilide, taken in connection with its pronounced physical resemblance to phenacetin, has already suggested to the unscrupulous the possibility of partial or even complete substitution of the former drug for the latter, and indeed several flagrant instances of such practice are on record. Accordingly, much time and effort have been expended in various quarters in the hope of devising a quantitative separation, though hitherto apparently without marked success. It is evident, however, that any procedure, calculated to determine even approximately the relative proportions of acetanilide and phenacetin in admixture, thus blocking the ways of the sophisticator, must prove welcome to officials and chemists engaged in drug control.

Ordinarily, the preliminary or gross separation of these two drugs from complex mixtures presents no unusual difficulties, being easily effected by extraction with chloroform. It is in the subsequent quantitative partition of the mixture thus isolated where the real problem begins, since no purely physical method, involving, for example, water or any of the commonly available organic solvents, lends itself to a sharp separation. A partial separation may indeed be effected according to Will<sup>2</sup> with water about as follows: If 1 gram of a mixture of equal parts of acetanilide and phenacetin be shaken with 200 cc. of water, all of the acetanilide goes into solution together with 0.13 g. of phenacetin, the remainder being unaffected. This latter portion is then filtered and weighed. Its weight, corrected by the addition of 0.13, represents the phenacetin originally present in this particular

<sup>1</sup>Thompstone, E., "Bat Guano in Burma," *Agr. J. India*, 4 (1909), 379-81.

<sup>2</sup>It has been reported that the "flight of the bats on leaving the cave, in rope-like formation, as large in diameter as an ordinary street car, requires over an hour, by actual timing."

<sup>3</sup>For further description see, Tod, W., "Ueber Fledermausguano," *Landw. vers. Station*, 1 (1859), 264-268.

<sup>4</sup>"Quotation on Nitrogen of Bat Guano," *Bull. Texas Exp. Station*, 160, July, 1913, p. 10.

<sup>1</sup>Chief, Synthetic Products Laboratory.

<sup>2</sup>*Pharm. J.*, [3] 21, (1890), 377.

mixture. In two similar experiments, but involving slightly different proportions of the two constituents, it was found that the weight of the undissolved phenacetin augmented by 0.13 corresponded to the quantity of this drug present in the mixture. It is quite evident, however, that such a procedure, while having a legitimate place in proximate determinations, could hardly form the basis for the quantitative separation of unknown mixtures.

In the method presently to be described, advantage is taken of the fact that, when an aqueous solution of phenacetin is added to a solution of iodine and potassium iodide containing a mineral acid, an iodine addition product or periodide separates, at first in an apparently emulsified condition, later assuming with greater or less rapidity—depending on temperature, concentration, and other undetermined factors—the form of brilliant bronze-colored leaflets, practically insoluble in the resulting menstruum, and having the composition<sup>1</sup>  $(C_8H_5O.C_6H_4.NH.COCH_3)_2.HI.I_4$ .

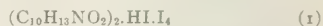
Acetanilide under like treatment yields no insoluble periodide, though there may be and doubtless is present in the resulting solution an iodine addition product of corresponding form,<sup>2</sup>  $(C_6H_5NH.COCH_3)_2.HI.I_4$ . If, therefore, the precipitation of the periodide is effected in a measured volume of standard iodine and the insoluble addition product then removed by filtration, it readily becomes possible to determine volumetrically the quantity of iodine thus withdrawn from solution and, by means of appropriate factors, calculate the phenacetin present in the mixture. The phenacetin may also be determined gravimetrically after liberation from its periodide and subsequent extraction with chloroform. The acetanilide is estimated in an aliquot of the filtrate from the insoluble periodide by extraction with chloroform—the free iodine having been first discharged with a sulfite—followed by hydrolysis with dilute sulfuric acid and final titration of the resulting aniline sulfate with standard potassium bromide-bromate.

#### EXPERIMENTAL

In practice, the mixture of acetanilide and phenacetin dissolved in very dilute acetic acid is added to standard iodine contained in a graduated glass-stoppered flask, in preference to the reverse operation, the resulting liquid being then acidified with hydrochloric acid. This order of procedure is the outcome of results obtained in a variety of experiments and based on the following considerations:

The chemical and physical properties of the periodide are such that the determination to be quantitative must be made in a relatively restricted volume, that is, in rather concentrated solution, but on the other hand, owing to the very slight solubility of phenacetin in aqueous media, the transfer of this substance in solution to that of iodine in the graduated flask, as also its retention therein in dissolved condition,

is a matter requiring very nice manipulation, since any premature separation of phenacetin as such from the resulting menstruum would necessarily lead to a corresponding loss in periodide formation and thus vitiate the determination. The small quantity of acetic acid employed not only facilitates solution of both phenacetin and acetanilide, but also inhibits latent hydrolytic tendencies affecting the acetyl group. Now it so happens that phenacetin yields with iodine and hydriodic acid not only the periodide.



on the formation of which the separation of acetanilide and phenacetin is based, but under certain conditions also a less insoluble addition product, containing one-half as much iodine,



While the former of these two periodides represents the optimum in iodine addition, constituting as it does the sole or major portion of the addition product as ordinarily obtained, the more the iodine content of the reacting medium is reduced by the separation of the favored type (1), the greater the tendency for the formation of type (2). Furthermore, since the separation of any periodide of the phenacetin type is conditioned on the presence of free hydriodic acid (or what amounts to the same thing, potassium iodide and hydrochloric acid), it is quite evident that a maximum homogeneity in the precipitated product can result only by first bringing the phenacetin, iodine and potassium iodide into such uniform distribution and intimate relationship that, on the rapid addition of hydrochloric acid, an immediate liberation of hydriodic acid required to complete the combination will take place simultaneously throughout the entire mass. With due regard, therefore, for the conditions set forth above, as also for errors naturally inherent in iodometric operations, it becomes possible to reduce to a minimum certain of these disturbing elements which might otherwise seriously impair the efficiency of the method.

In order to determine experimentally the most favorable conditions under which to operate, in any analytical procedure, it became necessary to carry through several hundred estimations, both singly and in series, a few of which appear below. With exception of Series 2, in which 25, 30, and 35 cc. of standard iodine were, respectively, used in the three determinations, 25 cc. of iodine were invariably employed.

#### Series 1

No.	Phenacetin Gram	Glacial AcOH Cc.	Conc. HCl Cc.	Iodine		Phenacetin	
				Excess Cc.	Expanded Cc.	recovery Gram	Per cent
1.....	0.2000	1.00	3 cc.	19.23	21.84	0.1959	97.95
2.....	0.2000	0.75	3 cc.	19.20	21.90	0.1964	98.20
3.....	0.2000	0.50	3 cc. H <sub>2</sub> SO <sub>4</sub>	19.20	21.90	0.1964	98.20
4.....	0.2000	1.00	2 cc. H <sub>2</sub> PO <sub>4</sub>	19.15	22.00	0.1973	98.65
5.....	0.2000	1.00	2 cc.	19.45	21.40	0.1932	96.60

#### Series 2

No.	Phenacetin Gram	Acetanilide Gram	Glacial AcOH	Conc. HCl	Excess Cc.	Iodine		Phenacetin		Acetanilide	
						Ex- pended Cc.	recovery Gram	Per cent	recovery Gram	Per cent	
1....	0.1200	0.0960	3	5	20.90	11.25	0.1197	99.75	0.0940	97.92	
2....	0.1200	0.0960	3	5	25.81	11.08	0.1179	98.25	0.0944	98.33	
3....	0.1200	0.0960	3	5	31.02	11.11	0.1182	98.50	0.0952	99.17	

<sup>1</sup>A more detailed description of the properties of this addition product—which was first described, though incorrectly interpreted, by Scholvin, *Pharm. Zeitschrift*, **32** (1891), 311—will appear shortly in a paper entitled "Periodides of Phenacetin, Methacetin and Triphenin."

Wheeler and Walden, *Am. Chem. J.*, **18**, 89.



Series 3		Phenacetin Gram	Acetanilide Gram	Glacial AcOH Ratio	Conc. HCl Cc.	Phenacetin recovery Gram	Per cent	Acetanilide recovery Gram	Per cent
1.....	0.2000	1	1	3	19.02	21.83	0.1976	98.83	
2.....	0.2000	1	1	3	19.25	21.37	0.1934	96.70	
3.....	0.2000	0.0500	4	1	3	19.18	21.51	0.1947	97.35
4.....	0.2000	0.1000	2	1	3	19.10	21.67	0.1961	98.15
5.....	0.2000	0.1500	1	1	3	19.02	21.83	0.1983	99.50
6.....	0.2000	0.2000	1	1	3	18.90	22.07	0.1994	99.70
7.....	0.1500	0.2000	3	4	3	21.76	16.35	0.1480	98.67
8.....	0.1000	0.2000	1	2	3	24.50	10.87	0.0984	98.40
9.....	0.0500	0.2000	1	4	3	27.60	4.67	0.0423	84.60
Series 4		Phenacetin Gram	Acetanilide Gram	Glacial AcOH Ratio	Conc. HCl Cc.	Phenacetin recovery Gram	Per cent	Acetanilide recovery Gram	Per cent
1.....	0.2000	1	1	3	19.00	21.87	0.1977	98.85	
2.....	0.2000	1	1	3	19.25	21.37	0.1932	96.60	
3.....	0.2000	0.0400	5	1	3	19.06	21.75	0.1966	98.30
4.....	0.2000	0.0500	4	1	3	19.05	21.77	0.1968	98.40
5.....	0.2000	0.0667	3	1	3	19.06	21.75	0.1966	98.30
6.....	0.2000	0.1000	2	1	3	18.94	21.99	0.1988	99.40
7.....	0.2000	0.2000	1	1	3	18.70	22.47	0.2028	101.40
8.....	0.2000	0.0500	1	4	3	24.38	11.11	0.1004	100.43
9.....	0.0667	0.2000	1	3	3	26.42	3.03	0.0636	95.30
10.....	0.0500	0.2000	1	4	3	27.36	3.15	0.0466	93.20
11.....	0.0400	0.2000	1	5	3	28.13	3.61	0.0326	81.50
Series 5		Phenacetin Gram	Acetanilide Gram	Glacial AcOH Ratio	Conc. HCl Cc.	Phenacetin recovery Gram	Per cent	Acetanilide recovery Gram	Per cent
1.....	0.2000	1	1	3	19.01	21.85	0.1975	98.75	
2.....	0.2000	1	1	3	19.22	21.43	0.1937	96.86	
3.....	0.2000	0.0400	5	1	3	19.10	21.67	0.1959	97.95
4.....	0.2000	0.0500	4	1	3	19.02	21.83	0.1973	98.67
5.....	0.2000	0.0667	3	1	3	19.04	21.83	0.1981	99.05
6.....	0.2000	0.1000	2	1	3	18.91	22.05	0.1993	99.67
7.....	0.2000	0.2000	1	1	3	18.75	22.37	0.2022	101.11
8.....	0.1000	0.2000	1	2	3	24.32	11.23	0.1015	101.52
9.....	0.0500	0.2000	1	4	3	27.40	5.07	0.0458	91.55
Series 6		Phenacetin Gram	Acetanilide Gram	Glacial AcOH Ratio	Conc. HCl Cc.	Phenacetin recovery Gram	Per cent	Acetanilide recovery Gram	Per cent
1.....	0.2000	1	1	3	19.02	21.83	0.1973	98.67	
2.....	0.2000	1	1	3	19.15	21.57	0.1950	97.50	
3.....	0.2000	0.0200	10	1	3	19.10	21.67	0.1959	97.95
4.....	0.2000	0.0400	5	1	3	19.04	21.83	0.1981	99.05
5.....	0.2000	0.0500	4	1	3	18.95	21.97	0.1986	99.30
6.....	0.2000	0.0667	3	1	3	18.90	22.07	0.1995	99.75
7.....	0.2000	0.1000	2	1	3	18.76	22.35	0.2020	101.02
8.....	0.2000	0.2000	1	1	3	18.60	22.67	0.2039	102.46
9.....	0.1500	0.2000	3	4	3	21.25	17.37	0.1370	104.67
10.....	0.1000	0.2000	4	2	3	24.25	11.37	0.1028	102.78
11.....	0.0500	0.2000	1	4	3	27.60	4.67	0.0422	84.43
Series 7		Phenacetin Gram	Acetanilide Gram	Glacial AcOH Ratio	Conc. HCl Cc.	Phenacetin recovery Gram	Per cent	Acetanilide recovery Gram	Per cent
1.....	0.2000	1	1	3	16.12	19.26	0.1978	98.90	
2.....	0.2000	1	1	3	16.40	19.06	0.1957	97.85	
3.....	0.1800	0.0200	9	1	3	17.08	17.34	0.1781	98.93
4.....	0.1600	0.0400	4	1	3	18.02	15.46	0.1588	99.23
5.....	0.1400	0.0600	3	1	3	19.34	13.62	0.1393	99.93
6.....	0.1200	0.0800	3	2	3	19.93	11.67	0.1195	99.62
7.....	0.1000	0.1000	1	1	3	20.90	9.70	0.0996	99.62
8.....	0.0800	0.1200	2	3	3	21.80	7.90	0.0811	101.41
9.....	0.0600	0.1400	3	7	3	22.80	5.90	0.0506	100.99
10.....	0.0400	0.1600	4	7	3	24.02	4.46	0.0389	88.83
11.....	0.0200	0.1800	1	9	3	25.32	0.86	0.0088	44.16
Series 8		Phenacetin Gram	Acetanilide Gram	Glacial AcOH Ratio	Conc. HCl Cc.	Phenacetin recovery Gram	Per cent	Acetanilide recovery Gram	Per cent
1.....	0.2000	1	1	2	16.30	18.90	0.1911	97.05	
2.....	0.2000	1	1	2	16.40	19.06	0.1921	96.05	
3.....	0.1800	0.0200	9	1	2	17.15	17.20	0.1766	98.13
4.....	0.1800	0.0200	9	1	2	17.30	16.90	0.1756	97.53
5.....	0.1600	0.0400	4	1	2	18.12	15.26	0.1567	97.95
6.....	0.1600	0.0400	4	1	2	18.20	15.10	0.1551	96.92
7.....	0.1400	0.0600	3	2	2	18.93	13.64	0.1367	100.06
8.....	0.1400	0.0600	3	2	2	19.12	13.26	0.1362	97.27
9.....	0.1200	0.0800	3	2	2	19.93	11.64	0.1195	99.62
10.....	0.1200	0.0800	3	2	2	20.02	11.46	0.1177	98.68
11.....	0.1000	0.1000	1	1	2	20.98	9.84	0.0980	97.98
12.....	0.1000	0.1000	1	1	2	21.00	9.50	0.0976	97.57
13.....	0.0800	0.1200	2	3	2	21.90	7.70	0.0791	98.85
14.....	0.0800	0.1200	2	3	2	22.05	7.40	0.0760	94.99
15.....	0.0600	0.1400	3	7	2	22.92	5.60	0.0573	95.85
16.....	0.0600	0.1400	3	7	2	23.04	5.42	0.0557	92.77
Series 9		Phenacetin Gram	Acetanilide Gram	Glacial AcOH Ratio	Conc. HCl Cc.	Phenacetin recovery Gram	Per cent	Acetanilide recovery Gram	Per cent
1.....	0.2000	1	1	3	16.20	19.10	0.1962	98.10	
2.....	0.2000	1	1	3	16.22	19.06	0.1957	97.85	
3.....	0.1800	0.0200	9	1	2	17.30	16.90	0.1736	96.42
4.....	0.1800	0.0200	9	1	2	17.05	17.40	0.1787	99.28
5.....	0.1600	0.0400	4	1	2	18.18	15.14	0.1555	97.17
6.....	0.1600	0.0400	4	1	2	18.20	15.10	0.1546	96.95
7.....	0.1400	0.0600	3	2	2	19.17	13.16	0.1332	98.34
8.....	0.1400	0.0600	3	2	2	18.96	13.38	0.1395	99.62
9.....	0.1200	0.0800	3	2	2	20.00	11.50	0.1181	98.42
10.....	0.1200	0.0800	3	2	2	19.90	11.70	0.1202	100.13
11.....	0.1000	0.1000	1	1	2	20.92	9.66	0.0992	99.21
12.....	0.1000	0.1000	1	1	2	20.90	9.70	0.0996	99.62
13.....	0.0800	0.1200	2	3	2	22.12	7.26	0.0746	93.20
14.....	0.0800	0.1200	2	3	2	21.90	7.70	0.0791	98.85
15.....	0.0600	0.1400	3	7	2	23.00	5.80	0.0566	94.14
16.....	0.0600	0.1400	3	7	2	22.90	5.70	0.0585	97.56
17.....	0.0400	0.1600	4	7	2	24.85	1.80	0.0185	46.21
18.....	0.0400	0.1600	4	7	2	24.22	3.06	0.0314	78.56

## INTERPRETATION OF RESULTS

As the title of this paper implies, the procedure comprehends in its entirety not only the separation but the estimation as well of both acetanilide and phen-

acetin. Accordingly, several of the mixtures examined were treated with this object in view, namely, the recovery of both ingredients, as embodied in Series 2. As a rule, however, analysis ended with the recovery of phenacetin, since this was believed to represent the more important phase of the problem under investigation. Examination of the data presented in the several series, as also that of other series not here shown, leads to the following conclusions:

Any mineral acid unaffected by iodine or hydriodic acid under the conditions of the experiment can apparently be employed, although hydrochloric acid is perhaps, on account of its physical properties, the one best suited to the purpose in hand. It will be noted that an increase of this acid within reasonable limits operates favorably on phenacetin recovery. In the estimation of this substance alone, not more than 200 mg. should be taken for every 25 cc. of standard iodine of specified strength, while the amount of acetic acid used in each determination should not exceed 1 cc., in which event the recovery will fall within 3 to 5 mg. of the quantity taken or actually present. In admixture with acetanilide, however, the total amount of both ingredients taken for analysis should likewise not exceed 200 mg., but more acetic acid may be advantageously employed, since such increase tends to counteract an apparent tendency on the part of acetanilide to augment unduly the quantity of phenacetin recovered. Whatever the cause of such excess recovery, whether due to occlusion or adsorption of iodine as such or in form of acetanilide periodide on the part of phenacetin periodide, the limit of usefulness of the method appears to lie between the ratios 1 : 3 and 1 : 4 of phenacetin to acetanilide. In order to observe what influence, if any, freshly boiled distilled water might have on phenacetin recovery, all estimations recorded in Series 9, with the exception of No. 1, were made with water thus treated. A comparison of recoveries noted under estimations Nos. 1 and 2 reveals a slight difference, it is true, apparently in favor of ordinary distilled water, that is, that from which the air had not been expelled, but such difference, conceivably due to the action of dissolved atmospheric oxygen or hydriodic acid, may have been the result of entirely different influences.

## METHOD

PHENACETIN.—Into a small (50 cc.) lipped Erlenmeyer introduce 0.2 g. of the phenacetin-acetanilide mixture, add 2 cc. of glacial acetic acid, heat gently over wire gauze to complete solution, then dilute with 40 cc. water previously warmed to 70°. Transfer the clear acetous liquid by pouring and careful washing of flask with two 10 cc. portions of warm (40°) water to a glass-stoppered, graduated 100 cc. flask, into which have been previously run from a burette 25 cc. of standard iodine, of a strength slightly above 0.2 *N*, and warmed to 40°. Rotate the resulting meniscus to uniformity, the flask being closed meanwhile, then add 3 cc. of concentrated hydrochloric acid, close flask anew and continue rotation until copious crystallization is apparent, then set the product aside to cool. If the ratio of phenacetin to acet-

anilide is equal to or greater than 1, the formation of crystalline scales will be almost immediate on the addition of acid. As the proportion of acetanilide increases, however, the periodide is not only more inclined to maintain the liquid state, with the result that crystallization becomes proportionately slower, but its separation also from the menstruum itself is in a measure apparently retarded. In such cases, gentle agitation of the liquid or rotation of the flask in water warmed to 40° or less tends to promote the formation of crystals. When the contents of the flask have assumed the room temperature, fill with water to within 2 to 3 cc. of the mark, rotate to uniformity and allow to stand overnight. Fill to mark with water, mix thoroughly, then after standing one-half hour withdraw a 50 cc. aliquot of clear liquid by passing through a small (5.5 cm.) dry, closely-fitted filter into a graduated 50 cc. flask, rejecting, however, about 15 cc. of the first runnings, the latter being received in any convenient container for eventual later use, along with additional filtrate, for the recovery of acetanilide. Transfer the 50 cc. aliquot by pouring and washing to a 200 cc. Erlenmeyer and titrate with 0.1 *N* sodium thiosulfate.

If reference is had to the composition of the insoluble addition product, constituting the basis for the foregoing separation,



it will be noted that, for every molecule of phenacetin involved, two atoms of iodine are required, hence from a titrimetric standpoint one atom of iodine is equivalent to one-half molecule of phenacetin. If, therefore, the quantity of iodine expended in the formation of insoluble periodide is ascertained as the result of such titration, the quantity of phenacetin thereby involved is readily calculated from the expression,

$$\text{phenacetin} = I(0.008890 \times N),$$

in which 0.008890 represents the quantity of phenacetin in 1 cc. of a 0.1 *N* solution of this substance, *N* the normality of standard thiosulfate employed, while *I* represents the number of cubic centimeters of such thiosulfate corresponding to the iodine entering into combination with phenacetin isolated as periodide.

The gravimetric determination of phenacetin may, if desired, be effected substantially as follows: In the operation of filtering off the periodide, the latter is collected on the filter and washed with 10 to 15 cc. of standard iodine solution, preferably by suction, then transferred together with filter (likewise any particles of precipitate eventually remaining in the graduated flask) to a separatory funnel, using for the purpose not over 50 cc. of water. After discharging both free and added iodine with a few small crystals of sodium sulfite, the liquid is extracted with three 50 cc. portions of chloroform, each portion being subsequently washed in a second separatory funnel with 5 cc. of water. After washing and clearing, withdraw solvent through a small (5.5 cm.) dry filter into a 200 cc. Erlenmeyer, distill off most of the chloroform, transferring the residual 5 to 10 cc. by pouring and washing with fresh solvent to a small tared beaker

or crystallizing dish. Evaporate to dryness on steam bath, cool, and weigh.

**ACETANILIDE**—Should the combined weight of the phenacetin-acetanilide mixture be known, that of the latter constituent can be determined by difference, or, if necessary, estimated directly from a second aliquot of filtrate from the phenacetin periodide.

To this end, transfer to a separatory funnel by means of a pipette 25 to 30 cc. of the clear liquid, decolorize with sufficient solid sodium sulfite, add solid sodium bicarbonate in slight excess, follow with 1 to 2 drops of acetic anhydride, then extract with three 60 cc. portions of chloroform, passing solvent when cleared through a small, dry filter into a 200 cc. Erlenmeyer, from which the chloroform is distilled by the aid of gentle heat down to about 20 cc. Now add 10 cc. of dilute sulfuric acid (1 cc. of concentrated acid to 10 cc. of water) and digest product on steam bath until the aqueous residue has been reduced one-half, add 20 cc. of water and continue digestion one hour, add a second 20 cc. portion of water and 10 cc. of concentrated hydrochloric acid, then titrate very slowly, drop by drop, with standard potassium bromide-bromate (1 cc. of which is equivalent to 5 to 10 mg. of acetanilide), until a faint yellow coloration persists. While adding this reagent, the flask should be rotated sufficiently to agglomerate the precipitated tribromoaniline and thus clarify the supernatant liquid. The number of cubic centimeters of standard bromide solution required to complete the precipitation, multiplied by the value of 1 cc. in terms of acetanilide, will give the quantity of this substance present in the aliquot taken.

#### COMMENT AND SUGGESTIONS

The preliminary or gross separation of phenacetin and acetanilide from complex mixtures is materially lengthened, if the preparation contains, in addition to those substances, caffeine or antipyrin or both, in which event it would be necessary first to subject the mixture of four ingredients to hot digestion with dilute sulfuric acid in order to convert phenacetin and acetanilide to phenetidine and aniline sulfates, respectively, from which caffeine and antipyrin may be easily separated by means of chloroform, after which operation phenacetin and acetanilide should be regenerated by treating the aqueous-acid solution of the corresponding sulfates with solid sodium bicarbonate in slight excess, thereupon with a few drops of acetic anhydride, followed by extraction with chloroform.<sup>1</sup>

In the operation of transferring the acetous solution of phenacetin-acetanilide mixture to the graduated flask containing standard iodine, great care must be exercised to the end that none of the dissolved substances crystallize out as such during or after the transfer, either in the liquid or about the neck of the Erlenmeyer, since any undissolved phenacetin introduced into the iodine reagent would fail in obtaining its full complement of iodine, thus vitiating the determination. The necessary transfer is most conveniently effected, and indeed without loss, by the use of an Erlenmeyer provided with a lip, a form easily

<sup>1</sup> Proc. A. O. A. C., U. S. Dept. Agr., Bur. Chem., Bull. 162 (1912), 197.

made in the laboratory from the ordinary type by heating the neck of flask in a moderate blast flame, then by the aid of a file or other suitable instrument pulling down the rim to the desired pitch. Thus modified, the flask delivers aqueous solutions with little or no tendency to run down on the outside of neck.

The standard solution of iodine employed in the foregoing separation and the one giving the best results has a strength slightly above 0.2 *N*, that is, a solution containing 30 g. of iodine and 40 g. of potassium iodide to the liter. To prepare, dissolve the potassium iodide in the least possible quantity of water, add the iodine and after complete solution, dilute to 1 liter. Twenty-five cc. of this reagent, the volume taken for each determination, are standardized with a solution of sodium thiosulfate containing 30 g. to the liter, the value of which has in turn been ascertained by titration with very carefully purified iodine. The end point is best observed by adding to the liquid toward the close of titration 1 to 2 drops of freshly prepared starch solution. In measuring off the standard iodine, make readings by the aid of transmitted light. This is easily done by holding an electric bulb just back of the burette, thus bringing into sharp relief the lower meniscus.

For this and similar iodometric operations, very pure iodine was prepared by dissolving the commercial resublimed product in concentrated aqueous potassium iodide, pouring the clear liquid into a large volume of water, filtering and washing the finely precipitated iodine on a porous plate several times with water, then drying first in the air and finally in a desiccator over sulfuric acid, where it is kept for future use in a glass-stoppered weighing tube. To standardize the sodium thiosulfate, weigh out in a small glass capsule (about 1/2" high and 5/8" diameter), provided with a closely-fitting glass cap or stopper, about 0.3 g. of pure iodine, which together with capsule and cover are transferred to a 200 cc. Erlenmeyer, containing 0.5 g. of potassium iodide dissolved in 10 cc. of water. After complete solution, titrate the iodine with sodium thiosulfate, using 1 to 2 drops of starch solution as indicator.

In the qualitative examination of preparations or mixtures, of which phenacetin alone is a known or declared ingredient, suitable tests should be applied in order to verify the presence or absence of acetanilide, such as are prescribed in the U. S. Pharmacopoeia or described in Allen's "Commercial Organic Analysis." For the identification of phenacetin, either alone or in admixture with acetanilide, the following test in addition to those ordinarily employed for this substance will be found of value: To 1 to 2 mg. of sample in a test tube add a drop of acetic acid, 0.5 cc. of water and 1 cc. of 0.1 *N* iodine, warm mixture to about 40°, then add a drop of concentrated hydrochloric acid. Almost immediately if phenacetin alone is present, or on cooling and agitating the liquid if sample consists in large part of acetanilide, the iodine addition product of phenacetin separates in the form of reddish brown leaflets or needle-like crystals. In the presence of considerable acetanilide, the periodide first separates as minute oily globules, which on vigorous

shaking gradually become crystalline aggregates. This test is so delicate that as little as 0.5 mg. of phenacetin may, if alone, be detected in form of its characteristic periodide.

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### COMMERCIAL PAPAIN AND ITS ASSAY

By H. M. ADAMS

Received April 24, 1914

A recent article by William Mansfield<sup>1</sup> gives a clear idea of the cultivation, preparation and adulteration of the commodity papain. The adulteration from the commercial standpoint is especially interesting, in view of the fact that about 50 per cent of the samples received were found to possess so little digestive power that they are practically worthless. It has long been noticed in this laboratory that the dark, lumpy samples invariably give the best digestive strength. It seemed that the darker, the more crude the appearance, the better they were. Occasionally a comparatively light colored sample would show a fair degree of activity, but such an occurrence was very rare indeed. This led to an investigation, with the result that in the poor samples starch was always found to be present in very marked quantities, while good samples showed no perceptible trace. Mansfield corroborates this with his statement that a large portion of the papain on the market is adulterated by adding wheat or rye bread crumbs or by pouring the papain juice over the breads and then grinding.

This discovery of starch instituted a preliminary test, which was applied to every sample of papain received. A small portion of the finely ground sample was placed on a white porcelain surface and a few drops of a weak solution of iodine added. The presence of starch was thus immediately noted by the appearance of a blue color and, with a little experience, a rough estimate could be made, by the intensity of this color, as to the digestive value of the sample.

To further illustrate this, a few experiments were carried out, showing the digestive strength of the papain and the amount of starch present. In these experiments a high-grade papain was used as a standard and called 100 per cent. The others are given in terms of this standard. The digestion was carried on at 55° C., with frequent shaking for five hours. Finely ground beefsteak was used as the material to be digested and distilled water as a medium.

SAMPLE	Cc. of residue standing 1 hour	Percentage as compared with standard	Percentage starch
Standard.....	5.25	100	
1.....	15	35	57.4
2.....	12.5	42	57.1
3.....	13	40	58.7
4.....	13	40	58.3
5.....	13	40	55
6.....	6	55.7	20
7.....	5.25	100	

It was observed in the above experiments that when large amounts of starch were present, the lower portion of the residue was white in color instead of having a greenish tinge as in the good samples.

Besides starch, pepsin is sometimes used as an adul-

<sup>1</sup> *J. Am. Pharm. Assoc.*, 1914, p. 169.



terant and is rather more difficult to detect. When tested in an acid solution a small amount of pepsin apparently greatly increases the strength of the papain; however, if a neutral or slightly alkaline solution is used, the action of the pepsin is inhibited or checked completely and the true digestive value of the papain is thus obtained. This point is shown by the following experiments, in which a high-standard papain was used and known quantities of pepsin added. The digestion was carried on as stated before.

Sample 0.325 gram papain	Pepsin added (1 : 3000) Gram	Medium	Residue standing 1 hour Cc
1.....	0.1	Neutral	57½
2.....		Neutral	57½
3.....		0.2% HCl	24
4.....	0.1	0.2% HCl	13

There appear in the late literature but two methods for the assay of papain, one by H. Graber<sup>1</sup> and the other by Rippetoe.<sup>2</sup>

Graber's method differs from the one used by the author in only one point. He uses a 0.3 per cent solution of hydrochloric acid as a medium, instead of a neutral solution. This, however, proves to be a decided difference, for as shown by all the following experiments, no very satisfactory results were obtained in an acid medium. It is true there is some digestion, but the residue is large and seems to hang in suspension throughout the tube in such a way that it makes the readings rather indistinct. The residue settles very slowly and has a decidedly different appearance than in either neutral or alkaline solution, having a dark brown color instead of having a greenish tinge as in the others.

Rippetoe supports this inhibitory action of an acid solution in his article, and Martin in 1883 states that hydrochloric acid above 0.05 per cent destroys the digestive activity completely. This latter statement, however, is, in the opinion of the author, much too severe, for, as the following experiments will show, there appears to be considerable digestion in a 0.1 per cent acid solution, which, however, decreases as the strength of the acid is increased. In these experiments both meat and whites of eggs were used as the material to be digested.

10 grams of	Papain used Gram	100 cc. medium	Residue 1 hour Cc.	Residue overnight Cc.
Beef.....	None	0.3% HCl	33	31
Beef.....	0.325	0.3% HCl	28 indistinct	30
Beef.....	0.325	0.3% HCl	26 indistinct	30
Beef.....	0.325	Neutral	61½	51½
Egg.....	None	0.3% HCl	34	33
Egg.....	0.325	0.3% HCl	33	29½
Egg.....	0.325	0.2% HCl	30	28½
Egg.....	0.325	0.1% HCl	28	26
Egg.....	0.325	Neutral	15	14

Rippetoe used in his method the whites of eggs prepared as for the pepsin assay in the U. S. P. He also uses 40 cc. of a 0.1 per cent caustic soda solution as a medium. There appear to be no serious objections to this method except that it seems to be a large amount of unnecessary work and gives no better results. The residues are larger than with meat and the readings indistinct even after an hour's standing. In fact the author obtained more definite, clearer results, with

egg, if a medium of distilled water was used instead of an alkaline solution.

The following experiments were made to illustrate this and also the advisability of using 40 cc. of solution as a medium instead of 100 cc. It is shown that with meat 40 cc. has a deleterious effect but with egg it is slightly advantageous.

0.325 gram of papain used				
10 grams of	Medium	Cc.	Residue after 1 hour Cc.	Residue overnight Cc.
Beef.....	Neutral	100	61½	51½
Beef.....	Neutral	40	15	9½
Egg.....	Neutral	100	15	14
Egg.....	Neutral	40	14	13
Egg.....	0.1% NaOH	100	24 indistinct	17½
Egg.....	0.1% NaOH	40	15	13

The method found to be suitable to all samples and which has proved itself satisfactory by a great many trials, is outlined as follows:

Add 0.325 gram of the powdered sample of papain to 10 grams of fresh, lean, raw beef, which has been finely chopped or passed through a sausage grinder and placed in a 6-ounce wide mouth bottle. Now add 100 cc. of distilled water, stopper, and shake the bottle with contents thoroughly until the meat is entirely disintegrated. Place in a water bath at 50–55° C., for 5 hours, shaking gently 1 minute every 15 minutes. Pour the contents of the bottle into a long, graduated tube and allow the residue to settle.

Due to various changes in the conditions in carrying on this digestion (such as a different lot of meat or a fluctuation of the temperature of the bath) the same sample on different days was found to give a variable residue of from 5 to 7 cc. Therefore a papain shown to possess a high digestive strength was chosen as standard and two bottles containing the required amounts of this standard were placed in the bath with the samples to be tested and thus definite results could be obtained, the unknowns being reported in terms of the standard, as for instance, if the standard gave a residue of 6.3 cc. and the prospective sample 7 cc., it was reported as 90 per cent papain.

Below are given comparative results of the three methods discussed, Graber's, Rippetoe's and the above method.

0.325 gram of papain used—6 hours digestion					
METHOD	SOLUTIONS	Cc. SOLU- TION	SUBSTANCE DIGESTED	1 hour Cc.	Residue overnight Cc.
Graber's.....	0.3% HCl	100	Beef	130	32
				26	30
Rippetoe's.....	0.1% NaOH	40	White of egg	14	12
				14.5	13
X.....	Neutral	100	Beef	16	6.5
				6.25	6.5

#### SUMMARY AND CONCLUSIONS

Commercial papain is sometimes adulterated with starch or pepsin. The presence of starch is shown with iodine solution and the pepsin by digestion of meat in a weak acid solution.

Neutral solutions give the most satisfactory results with either meat or whites of eggs.

Meat appears to be the best material to be digested on account of its easy preparation and also because of the small residue left after digestion.

<sup>1</sup> THIS JOURNAL, 3 (1911), 120.

<sup>2</sup> *Ibid.*, 4 (1912), 517.

# A METHOD FOR THE ESTIMATION OF PODOPHYLLUM RESIN

By W. M. JENKINS

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It seems to be a generally acknowledged fact that the therapeutic activity of Podophyllum is due to the resin which it contains. While this resin is recognized in the United States Pharmacopoeia, and its properties and solubilities are well described, it must be remembered that the resin is not a simple substance, but a mixture of substances, the most important of which is a crystalline body called Podophyllotoxin. From a therapeutic standpoint, however, Podophyllum Resin, U. S. P., is a well known substance and the dose is well defined. It would seem therefore that any attempts at assaying or standardizing the drug should be in terms of Podophyllum Resin, U. S. P. It was with this idea in view that the work described in this paper was undertaken.

All previous methods for the determination of Podophyllum Resin have been based on the idea that the resin is insoluble in water, and that by pouring an alcoholic solution of the resin into a large volume of acidulated water the resin<sup>1</sup> would be completely precipitated and could be collected and weighed. Through long experience with this precipitation method, however, it has been found that the results are very unreliable and greatly affected by the conditions of the method, *viz.*, the volume and temperature of the acidulated water, the amount of alcohol used and the amount of sample taken. The only way to get results which were at all concordant was to adhere strictly to the same amounts of alcohol, water, acid and sample; the results were thus purely arbitrary.

The reason for these variable results was later found to be the fact that Podophyllum Resin is slightly soluble in water and that this solubility is increased by small percentages of alcohol, and hence the recovery of the full amount of resin by the precipitation method is impossible. Thus it was found that by dissolving 0.4 gram of U. S. P. Podophyllum Resin in 10 cc. of alcohol and precipitating the resin in 600 cc. of water acidulated with 10 cc. of hydrochloric acid, only 75 per cent of the resin was recovered.

Podophyllum Resin is only partly soluble in chloroform but is readily soluble in a mixture of 1 part of alcohol and 2 parts of chloroform. Hence it was thought that a mixture of alcohol and chloroform might be used for extracting the resin quantitatively from an alcohol solution which had been diluted with water.

When equal volumes of alcohol, chloroform and water are mixed, this mixture separates, on standing, into two layers. The upper portion consisting approximately of one part of alcohol and two parts of water, and the lower layer of one part of alcohol and two parts of chloroform.

By keeping the proportions of alcohol, chloroform and water constant, it was found that over 99 per cent of resin was recovered by three extractions with the alcohol chloroform mixture when working with U. S. P. Podophyllum Resin.

When this method was applied to the fluidextract, however, and the resulting resin compared with the U. S. P. Podophyllum Resin, it was found to be darker, more hygroscopic, less soluble in alcohol and more soluble in water. Thus it was necessary to modify the method in some way in order to obtain a resin identical with the official resin. This was accomplished by washing the alcohol chloroform extract with acidulated water. The resin obtained by this modification was found to conform to the United States Pharmacopoeia requirements for Podophyllum Resin, *viz.*:

Soluble in alcohol in all proportions.  
86.4 per cent soluble in ether.  
69.1 per cent soluble in chloroform.  
21.3 per cent soluble in boiling water.  
0.1 per cent ash.

By this procedure from 0.4 gram Podophyllum Resin U. S. P. dissolved in alcohol, 0.394 gram was recovered, corresponding to 98.4 per cent.

Accordingly the following method for estimating the amount of Podophyllum Resin in Fluidextract Podophyllum is suggested.

Measure 5 cc. of Fluidextract Podophyllum into a separatory funnel, add 5 cc. of alcohol, 10 cc. of chloroform and 10 cc. of acidulated water containing 0.6 per cent hydrochloric acid (2 cc. HCl in 100 cc. water). Shake and allow the mixture to separate. Draw off the lower layer into another separatory funnel; repeat the extraction twice, using 15 cc. of a mixture of one part of alcohol and two parts of chloroform, each time, and add these extractions to the first. Shake the combined extractions with 10 cc. of the acidulated water and allow the mixture to separate. Draw off the lower layer into a tared flask, and repeat the extraction twice, using 15 cc. of the alcohol chloroform mixture each time. Evaporate the combined extractions and dry the residue to constant weight at 100° C.

For comparison a number of fluidextracts were assayed by this method, and by the usual precipitation method with the following results:

	RESIN IN FLUIDEXTRACTS			
	Precipitation method G. in 10 cc.	Per cent	Shake-out method G. in 5 cc.	Per cent
1.....	0.424	4.2	0.3480	6.9
2.....	0.420	4.2	0.3130	6.2
3.....	0.420	4.2	0.2895	5.7
4.....	0.458	4.5	0.3430	6.8

In assaying the drug, 10 grams in a No. 60 powder are placed in an Erlenmeyer flask, and 25 cc. of alcohol are added. The flask is then fitted with a stopper through which is inserted a glass tube about two feet long for a condenser and left on a sand bath at 80° C. for three hours.

The contents of the flask are then transferred to a small percolator and washed with alcohol until about 50 cc. of percolate are obtained. When cooled to room temperature, the solution is made up to exactly 50 cc. Of this solution, 10 cc., representing 2 grams of the drug, are used for assay, which is carried out in exactly the same way as described for the fluidextract, with the exception of the addition of the 5 cc. of alcohol, which is omitted.

It was found that it required at least 48 hours macer-

<sup>1</sup> J. Chem. Soc. (Trans.), 1898, p. 209

ation with cold alcohol to exhaust the drug, and hence the hot maceration is advisable.

Six different samples of Podophyllum were assayed by this method, and from the same samples fluid-extracts were made according to the directions in the United States Pharmacopoeia, and were also assayed. The results are given below:

	Grams resin in 100 grams drug	Grams resin in 100 cc. fluidextract
1.....	5.03	4.96
2.....	5.24	5.16
3.....	4.65	4.66
4.....	4.92	4.89
5.....	4.73	4.83
6.....	6.82	6.71

These results show that the method gives very concordant results on the assay of the drug and fluidex-

tract and much higher results than the precipitation method. If the method gives equally good results in the hands of other workers, then it would be advisable that fluidextract of Podophyllum, U. S. P., be assayed and standardized. As good lots of Podophyllum drug contain 5 per cent of resin, a standard of 5 per cent resin for the fluidextract is suggested.

The method can also be applied to the assay of solid and powdered extracts of Podophyllum by dissolving weighed quantities of the extracts in sufficient alcohol to render the solutions of about the same strength as fluidextract.

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## LABORATORY AND PLANT

### STUDIES ON FILTRATION<sup>1</sup>

By J. W. BAIN AND A. E. WIGLE

In connection with factory operation quite recently, one of the authors had to form an estimate, in advance, of the amount of moisture which would be retained by a finely divided solid on a vacuum filter. A search among the usual sources of information yielded no serviceable data. When the filters were in actual operation, their performance in this respect was very much better than had been anticipated, and had this fact been known in advance some economy in construction might have been effected.

With a view to gaining information on this point, the authors investigated the literature at their disposal, and with the exception of the interesting and valuable paper by Hatschek,<sup>2</sup> they were unable to find any useful data. When the experimental work had progressed to a certain extent, an accident drew our attention to the exhaustive monograph of King and Slichter, "Principles and Conditions of the Movements of Ground Waters,"<sup>3</sup> from which we have drawn freely in this discussion.

In the problem which is here under investigation, the solid is assumed to be bathed by a liquid in which it is insoluble, such as, for instance, the mother liquor of a crystalline magma. It is proposed, therefore, to investigate the amount of liquid retained by a mass of finely divided solid when filtration is carried out under atmospheric or other pressure and also in the centrifuge.

The experimental work was considerably simplified by the condition laid down above, which permitted the use of a solid insoluble in water. A quantity of pure well-rounded lake sand was carefully sieved, and the grains which were retained on the 40 mesh screen but which passed the 30 mesh, are referred to throughout as 40 mesh sand. The screens used were not of very good quality in the regularity of the mesh opening, as will be seen from the data given later, but this point is of no particular significance in this investigation.

<sup>1</sup> Presented at the 6th Semi-annual Meeting of the American Institute of Chemical Engineers, Troy, New York, June 17-20, 1914.

<sup>2</sup> *J. Soc. Chem. Ind.*, 1908, p. 538.

<sup>3</sup> *Nineteenth Ann. Report*, U. S. Geol. Survey.

The rate of flow of a given liquid under a constant head through a filter-mass of a finely divided solid will obviously be dependent upon the amount of space which is not occupied by the grains, *i. e.*, what is commonly called the "pore space." On first consideration, it would appear that the pore space would vary a good deal according to the size of the grains composing the mass, and the results of computation and experiment are an astonishing contradiction to this idea. The pore space is almost independent of the size of the grains, and the arrangement of the latter is of chief importance. By considering a number of small spheres of uniform diameter packed as closely as possible in a given space, it is possible to arrive at a mathematical formula from which the pore space may readily be calculated.

Slichter<sup>1</sup> has shown that if the spheres are so arranged that their centers lie at the corners of a cube, the pore space will be 47.64 per cent; while if the centers of the spheres lie at the corners of a rhombohedron which permits the closest possible packing, the pore space is 25.95 per cent. Between these limits we may expect to find the porosities of all ordinary materials.

With actual materials, in the case where the grains are of approximately equal size, the pore space and also the diameter of the particles may be readily determined by counting a number of the grains, determining their combined weight and the specific gravity of the material; the total volume may be ascertained by adding the sand in small quantities to a cylinder, tapping gently with a flat-faced pestle until no further decrease in volume takes place. The results of this procedure on our sands are presented in Table I.

Mesh screen	No. of grains	Total wt. grm.	One grain wt. grm. $\times 10^3$	Sp. gravity	Pore space per cent	Diam. Mm.
30	(300)	0.0307	10.23	2.74	35.4	0.420
	(300)	0.0316	10.36			
40	(400)	0.0251	6.3	2.68	34.1	0.354
	(400)	0.0253	6.3			
50	(500)	0.0182	4.55	2.73	36.4	0.318
	(500)	0.0246	4.92			
60	(600)	0.0238	2.97	2.82	36.8	0.269
	(600)	0.0172	2.87			
80	(800)	0.0202	5.2	2.85	37.7	0.257
	(600)	0.0156	2.60			

The comparatively slight variation in pore space

<sup>1</sup> *Loc. cit.*, p. 309.



is worthy of note; and it may be added at this point that mixtures of small and large grains show a surprising similarity in their porosity to that of either taken alone. For all practical purposes, the pore space of masses of crystals, such as are commonly produced by rapid cooling, may be placed at 37 per cent of the total volume occupied.

#### FILTRATION UNDER ATMOSPHERIC PRESSURE

This part of the subject has been so carefully worked out by King<sup>1</sup> that it suffices to reproduce some of the results, slightly modified to suit the present purpose. Cylinders 8 feet long, 5 inches in diameter, were filled with special, sorted sands, wire gauze being used as a support at the bottom. Water was introduced from below, and when the tubes were full, percolation was allowed to commence, and the water which drained away was collected and weighed at intervals.

TABLE II

Effective size of grains Mm.	Pore space Per cent	Water retained per cent of dry sand	
		After 1 hour	After 9 days
0.4745	38.86	11.23	4.24
0.1848	40.06	12.72	5.05
0.1551	40.76	14.73	7.25
0.1183	40.57	19.30	9.41
0.0826	39.77	20.15	11.82

#### FILTRATION WITH VACUUM

Experiments were carried out by the authors with the idea of approximating to factory conditions.

The sand was poured into a Buchner funnel provided with a piece of wire gauze, and gently tamped down with a flat-faced pestle; the depth of the layer was  $1\frac{1}{4}$  inches. The top of the funnel was closed by a glass plate ground to fit and provided with a central aperture through which air could be admitted. To avoid the error of surface evaporation during filtration, this air was drawn through a tower, down which water trickled slowly. The funnel was placed in a suction flask and a simple gauge enabled the vacuum to be read. When the sand had been under vacuum for a given period, it was thoroughly mixed and a sample removed; water was once more poured on and the vacuum was maintained for a longer period. The results are given in Table III.

TABLE III  
Moisture at the end of

Mesh screen	Moisture at the end of			Vacuum In mercury
	5 min.	15 min.	30 min.	
30	7.20	5.69	4.78	1.5
40	8.20	6.84	5.19	1.25
50	8.65	7.50	6.41	0.75
60	8.42	7.38	6.90	2.0
80	9.15	7.52	7.37	2.25

It is seen from these results that the moisture content increases inversely as the diameter of the grains of sand. In each experiment the water pump was worked at full capacity, and as might be predicted, the vacuum increases slightly as the size of the grains decreases.

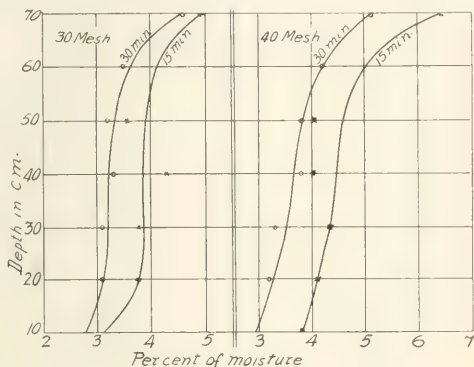
By way of comparison, a single experiment with sand of mesh 50 may be quoted. Water was poured on the layer and no vacuum was used; after 15 minutes' standing, the moisture content was found to be 27.4 per cent against the 7.50 per cent under vacuum.

The amount of liquid retained by different portions

<sup>1</sup> *Lon. fil.*

of a mass of grains in a filter, becomes important when the question of washing away an impure mother liquor has to be considered. A series of experiments was performed with the object of ascertaining the amount of water retained in the sands at different levels while under vacuum.

To carry this out, a tube about 80 cm. long and provided with side tubes closed with corks at 10 cm.



intervals, was filled with each sand, and connected as has been described in the case of the Buchner funnel. A powerful water pump was run to full capacity and the pressure, as before, varied with the size of the grain. The results are given in Tables IV and V.

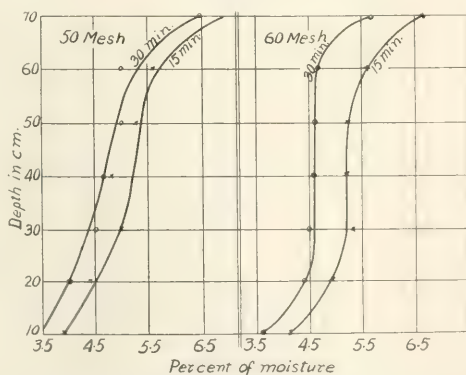
TABLE IV—PERCENTAGE MOISTURE AT END OF 15 MINUTES

Mesh screen	Pressure In mercury	Depth of sample from top in cm							Mean per cent moisture
		10	20	30	40	50	60	70	
30	4.5	3.13	3.78	3.77	4.28	3.56	4.13	4.90	3.97
40	4.0	3.82	4.10	4.33	4.08	4.08	5.08	6.45	4.60
50	6.5	3.90	4.40	5.00	4.80	5.30	5.60	7.60	5.30
60	7.0	4.14	4.95	5.32	5.20	5.20	5.63	6.60	5.30

TABLE V—PERCENTAGE MOISTURE AT END OF 30 MINUTES

Mesh screen	Pressure In mercury	Depth of sample from top in cm							Mean per cent moisture
		10	20	30	40	50	60	70	
30	4.5	2.84	3.08	3.10	3.31	3.19	3.51	4.56	3.35
40	5.0	3.03	3.24	3.30	3.76	3.83	4.20	5.13	3.85
50	6.5	3.40	4.00	4.50	4.65	4.95	5.00	6.50	4.70
60	7.0	3.58	4.37	4.56	4.60	4.60	4.65	5.75	4.70

These results were plotted and curves were drawn as shown in the accompanying illustrations. The



individual points were sometimes decidedly off the curves, but although the experiments were repeated in these cases, no better agreement could be obtained;

the accurate determination of small amounts of moisture in these sands proved to be difficult, probably owing to sampling. The average per cent of moisture was determined by measuring the areas under the curve, and dividing this by the height which gave the width of the rectangle of equal area.

#### FILTRATION WITH CENTRIFUGE

This well-known method of separating solids from liquids was next subjected to test for the sake of comparison with the previous experiments.

A small hand centrifugal,  $4\frac{1}{4}$  inches inside diameter, was used; it could be run at 5000 r. p. m. without any trouble. A cylinder of wire gauze,  $1\frac{3}{4}$  inches in diameter, was placed over the axis of the machine and the sand was poured into the annular space thus formed; the layer had, therefore, a thickness of  $1\frac{1}{4}$  inches which was the same as that in the Buchner funnel.

As a preliminary experiment, the sand was thoroughly wetted, and the centrifugal run at 2000 r. p. m. for 2 minutes. The percentages of moisture are given in Table VI.

Mesh screen	Vacuum 15 min.	Centrifugal 2 min.
50	7.50	2.56
60	7.38	2.55

The marked efficiency of the centrifugal is noteworthy and the method of procedure was altered to show this more forcibly.

Sand was placed in the Buchner funnel, wetted and vacuum applied for 5 minutes. After sampling, the sand was placed while still moist, in the centrifugal which was then run for 2 minutes at 2000 r. p. m. Table VII shows the percentages of moisture.

Mesh screen	Vacuum 5 min.	Centrifugal 2 min.
30	7.35 7.12	2.36 2.20
40	7.50 7.60	1.93 2.30
50	8.70 8.60	2.56 2.80
60	9.35 8.40	2.36 2.65
80	9.70 9.56	2.49 2.46

It is seen from the above results, that the moisture content under vacuum varies inversely as the diameter of the grains; the moisture content after centrifuging, however, is nearly the same for the finer as it is for the coarser sands.

The distribution of the water at several points in the annulus of sand was also investigated and Table VIII presents the results in percentage of moisture.

Mesh screen	Distance from center of basket		
	$\frac{1}{2}$ "	1"	$1\frac{1}{2}$ "
40	2.9	2.72	2.43
50	3.0	2.90	2.76

The variation, while sufficient to permit measurement, is small and might be neglected for practical purposes.

The objection may be raised that these results, obtained in the laboratory with a small centrifugal, are of little value for comparison with the larger machines used in the factory. While with the hand centrifugal, the diameter is small, the speed is high,

and we have calculated that a weight of 1 lb. revolving at a 2 inch radius at 2000 r. p. m. is subjected to practically the same centrifugal force as a weight of 1 lb. revolving at a radius of 12 inches at 600 r. p. m. The comparison is, therefore, justifiable and a good idea of the behavior of a moist mass when centrifuged in the factory, may be obtained beforehand in the laboratory.

Using the formula given by Griscom,<sup>1</sup> we have calculated the pressure as the periphery of the  $4\frac{1}{4}$  inch centrifugal running at 2000 r. p. m. and find it to be 7.66 lbs. per sq. in.

#### THEORETICAL CONSIDERATION

Hatschek<sup>2</sup> has discussed the behavior of very finely divided substances on the filter, and has pointed out the value of a microscopic examination in this connection. The probable arrangement of the particles, with respect to the pores of the septum, are pointed out, and the influence of the flexibility of the latter is taken into consideration.

The retention of small quantities of liquid in the mass of fine grains is due, undoubtedly, to capillarity. The extraordinary difficulty in removing the last few per cent is well known and is again set forth above. In considering the reasons for this, it seemed to be worth while to calculate what would be the thickness of the film, if all the residual water were assumed to be distributed uniformly over the superficies of the grains. For this purpose, sand of 30 mesh with 6 per cent moisture was selected; the thickness of the film of water on each grain was found to be 0.0116 mm.

It would be interesting to calculate what stress must be applied to a grain thus coated, to overcome the surface tension of the liquid in so far as to allow the removal of at least part of the water; such a computation, if it could be effected, might furnish a scientific basis for the prediction of the behavior of finely divided solids on centrifuging. The authors have been unable to find time to carry this out, but hope to do so in the future.

The above discussion assumes that all the water is present on the superficies of the grains, but the capillary action of the small spaces between the grains is undoubtedly of great importance. In the case of the sand just quoted, which has a pore space of 35.4 per cent, the moisture present would fill 30 per cent of this; that is, 70 per cent of the pore space is filled only with air. This gives some idea of the comparatively poor performance of the ordinary filter and of the vacuum filter; in each case, air channels form and the downward pressure on the water-filled pores is thus relieved. In the case of the centrifugal, each particle of water experiences practically the same stress, and only the capillarity of the finest pores and the surface tension of the films on the grains are sufficient to resist its action.

#### SUMMARY

1.—The pore space in a mass of fine grains averages about 37 per cent of the total volume.

<sup>1</sup> *Metal. and Chem. Eng.*, April, 1913.

<sup>2</sup> *Loc. cit.*

2—The amount of water retained when an ordinary filter is used varies from 11 per cent, with 20 mesh material, to 20 per cent with 100 mesh material, one hour being allowed for drainage.

3—The amount of water retained on a filter with 2 in. vacuum averages 7 per cent after 15 minutes for material varying from 30 to 80 mesh.

4—In a layer of material 70 cm. deep on a filter, with 5 in. vacuum, the top layer will average, after 15 minutes, 4 per cent moisture, and the bottom 6.5 per cent; the size of the grains is not of importance within the limits discussed. If the vacuum be maintained for 15 minutes longer, the above figures will be reduced by another half per cent.

5—By the use of a centrifugal, the percentage of moisture, in all the materials employed, may be reduced to an average of 2.5 per cent.

6—In the case of a sand of 30 mesh with 6 per cent moisture, if all the water be distributed over the surface of the particles, each grain would have a film 0.0116 mm. thick; or the water would fill 30 per cent of the pore space.

FACULTY OF APPLIED SCIENCE  
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### SCRUBBER FOR CHEMICAL LABORATORY VACUUM SYSTEM<sup>1</sup>

By CHARLES BASKERVILLE

In order to protect the vacuum pump of our laboratory from the corrosive action of the gases drawn therein, I devised the installation described herewith. The pump—an improved Packard Vacuum Pump, 2 cylinder, 12 in. diam., motor-belt driven—has been in more or less continuous service for seven years without any expenditure thereon for repairs, as a result of this protection. It seemed safe, therefore, to present an account of it.

The installation is an application of the simple principles usually applied on a small scale with glass apparatus in the laboratory.

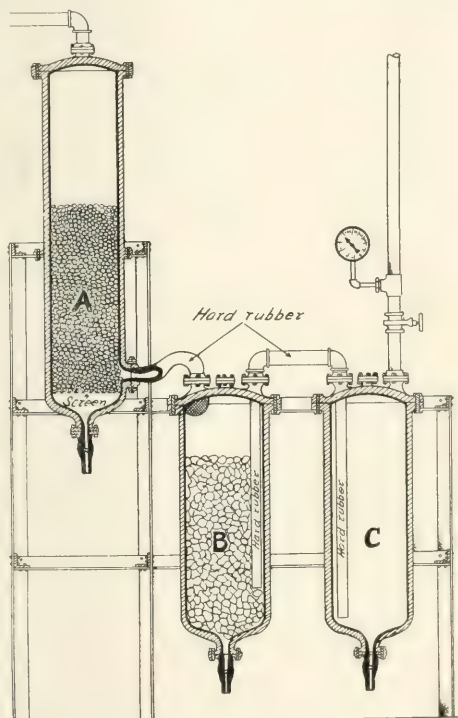
The towers are made of cast iron, porcelain-lined, and set into the system with a by-pass, which we have used only during the short time necessary for recharging. The towers are connected by hard rubber pipes (2 in. internal diameter). At the bottom of each tower is a hard rubber drain cock, bolted to a flange. At the top of *B* and *C* are plates bolted to flanges, which may easily be removed. The opening is of sufficient size to admit dropping a strung incandescent bulb for inspection.

Tower *B* is three-quarters filled with pumice stone in egg-size pieces. The pumice is thoroughly saturated with concentrated sulfuric acid. I believe lead pipe would be better in this cylinder as the hard rubber softened on contact with the acid. So far, however, the weight of the pumice and acid has not been sufficient to cause the hard rubber pipe to collapse. The decomposition of the rubber compound became so pronounced with the drain cock in a short while that it was replaced by a lead plate, which has proven satisfactory.

<sup>1</sup> Presented at the 6th Semi-annual Meeting of the American Institute of Chemical Engineers, Troy, New York, June 17-20, 1914.

factory. Incidentally, it may be stated that all efforts to get the hard rubber people to provide a material which would stand up against cold concentrated sulfuric acid have been futile. Hence, it may be well to warn others as to their claims in this respect. A pear-shaped screen of copper gauze was placed in the opening of Tower *B* leading to Tower *A* to prevent clogging, in the event a rushing action of the pump sucked pieces of the pumice. We draw off and replenish the acid once or twice a year.

Tower *A* is half filled with angular pieces of commercial caustic soda, in size from a hazel nut to an egg. The mass rests upon a copper wire gauze screen



SCRUBBER FOR CHEMICAL LABORATORY VACUUM SYSTEM—SCALE, 1 in. = 2 ft.  
A—Caustic Soda; B—Sulfuric Acid and Pumice; C—Trap

supported on and by the tapering bottom of the tower. The drain cock admits of drawing off any liquefied caustic which may accumulate. A metal pipe leads from the top to the pump.

Tower *C* is a safety reservoir to catch the fluid from *B* in the event of a leak beyond or other cause for increase in pressure on the pump side in the line. So far, no indication of its real need has been apparent, as the maximum and minimum contacts of the automatic regulator of the motor have never failed.

A gauge in the system beyond the scrubber serves, by comparison with the gauge on the pump, to show leaks in the scrubber. None was observed until the hard rubber drain cock on Tower *B* failed, and none



has been noted since the change described above, over six years ago.

The whole installation is supported on angle iron, painted with a rust-proof paint and may be inspected by members of the Institute any time.

COLLEGE OF THE CITY OF NEW YORK

## NEW APPARATUS FOR DETERMINATION OF HYDROGEN SULFIDE IN WATER - PART I

By GEO. B. FRANKFORTER

Received May 18, 1914

Hydrogen sulfide has been known with absolute certainty since the 15th century. It was first recognized in natural water under the name "sulfur vapors" and the water was known as "sulfur water." It was known to Paracelsus who studied sulfur carefully and used it extensively in his medical work. He must have known of its presence in certain natural waters.

Scheele, however, was the first to give exact knowledge concerning its properties. He designated it as a compound of sulfur, phlogiston and heat, and made an effort to determine the amount of sulfur in the gas.

Since Berthollet's classical work on its composition many methods have been employed for its quantitative determination. In general the methods of analysis are grouped into two classes, gravimetric and volumetric. The first exact method for its determination was given by Bunsen,<sup>2</sup> in which he used iodine. Bunsen recognized some of the difficulties in the method, for he states that the quantity of iodine used must be small for good results. He also noticed for the first time that hydrogen sulfide decomposes very readily so that the estimation is often not very exact. Since Bunsen's time the iodine or iodometric method has been modified so as to meet the different conditions under which the gas occurs. For instance, special apparatus and special modifications in the iodine method are necessary for its determination in illuminating gas, and special apparatus is necessary or at least highly desirable for its rapid determination in natural water as it decomposes when exposed to the air and light.

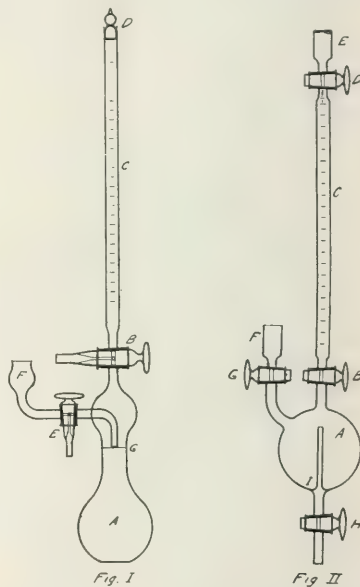
My attention was called to the fact that water from a sulfur spring, after it had stood for a day or so in a clear glass bottle—whether directly exposed to air and light or not—showed but a trace of gas, although it was present in the water in appreciable quantities when the sample was taken. I was aware that the gas, when dissolved in water containing air, readily decomposes liberating free sulfur, but I could hardly believe that the sulfur water hermetically sealed would change very rapidly if the water contained dissolved air.

In the case of a spring water containing approximately 1 cc. per liter, the gas was entirely dissociated in six hours after the sample had been taken from the spring. So rapid was the dissociation in this particular spring that it was quite impossible to obtain concordant results without making the analysis right at the spring.

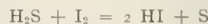
In order to do this, however, it was found necessary to carry considerable apparatus along, making the whole method quite unsatisfactory. I therefore experimented with a number of different forms of apparatus which could be carried around without difficulty, and which would simplify the process in such a way that it might be used for field service. After trying out a number of forms the two following were found to give perfectly satisfactory results.

Figure I consists of a flask, "A", which holds exactly 500 cc. of water when filled to "G". "C" is a burette with a stopper, "D," connected with flask "A" by means of a three-way cock, "B". "F" is a funnel tube also connected with "A" by means of a three-way cock "E".

Manipulation is as follows: The three-way cock "E" is turned so that the opening in the end of the cock is directly connected with "A." "B" is likewise



turned so that the opening in the end of the cock is connected with "A." The flask is then thrust into the water to be examined. Water enters "E" forcing the air out through "B" until the flask is full. On removing the flask, "E" acts as a siphon allowing the water to run out to the level "G". By this means exactly 500 cc. of water can be measured. Cock "E" is now turned a quarter way around, connecting funnel "F" with "A." One cc. of starch solution is introduced, "E" is closed and the water is titrated with standard iodine solution from burette "C." From the amount of iodine solution used the quantity of hydrogen sulfide may be calculated according to the following equation:



In rapid work, and especially in field work, it is very

<sup>1</sup> Ann. chim., 1791.

<sup>2</sup> Ann. Chem. Pharm., 86, 265.

essential that the quantity of gas be read off directly without calculations. In working out this method, therefore, a standard solution was so prepared that 1 cc. of the iodine solution would be equivalent to exactly 1 cc. of hydrogen sulfide gas, under normal conditions.

Figure II is the form which was finally adopted as giving most satisfactory results. It consists of a bulb, "A," which acts as the receiver, and which is connected at the bottom with a tube, "I," which extends up into the bulb so that when cock "H" is open bulb "A" will hold a definite quantity of water. The quantity which "A" will hold when exactly perpendicular is quite constant, at least enough for all ordinary purposes.

"B" is a stopcock connecting "A" with burette "C." "F" is an outlet necessary for filling the flask and for introducing starch solution as an indicator. "D" is a stopcock on the upper end of the burette connected with a funnel tube, "E." The latter is necessary for filling the burette and also for enclosing the standard iodine solution so that the apparatus may be shaken or even turned upside down without losing any of the solution.

The manipulation is as follows: Cocks "H" and "G" are opened, the apparatus is grasped by the burette and "A" is thrust into the water to be examined and held there until the bulb is full. It is

then withdrawn, held perpendicular until the water is on a level with the top of the tube "I." The quantity of water is therefore automatically measured, the tube being so adjusted that it measures 250 cc. Stopcock "H" is then closed and 1 cc. of starch solution introduced through "F." "G" is then closed and the water titrated with standard iodine solution from burette "C."

Calculations were made in the same manner as was described above for Fig. I.

With either of these forms, a sample of water may be taken directly from the spring or source of supply and a determination of hydrogen sulfide made in less than one minute.

As has already been stated, it was found that hydrogen sulfide decomposed much more readily than had been supposed. In some cases decomposition began in a few moments after taking the sample, as was indicated by opalescence due to free sulfur.

In order to test out the above forms of apparatus a great number of analyses were made. In addition to testing the apparatus, data concerning the rate of decomposition were obtained. Several series of experiments extending over a wide range I hope may appear in *THIS JOURNAL* in the near future.

SCHOOL OF CHEMISTRY  
UNIVERSITY OF MINNESOTA, MINNEAPOLIS

## ADDRESSES

### THE PRESENT PATENT SITUATION<sup>1</sup>

By MAXIMILIAN TOCH

On February 1, 1913, the new rules for procedure in patent litigation became effective, and after fifteen months a calm review of the benefits derived from the new rules is opportune. To those who are unacquainted with these new rules let me state briefly that the old custom of patent litigation was in taking of testimony before a Master in the office of either the defendant's or the plaintiff's attorney, and this Master came in to swear in each new witness, but never remained, and even if he did remain he had no authority to decide upon the propriety of the questions asked. The testimony was taken down invariably in long-hand. The costs were appalling, for the fees of a patent attorney are from \$50 to \$100 per day, the fees of the experts are the same, the cost of printing or typewriting is very great, and although it has often been said that no poor man can litigate a patent I know that no man in medium circumstances can fight one either, for in six months \$20,000 can disappear faster than ice under the midsummer sun.

The new rules in themselves are excellent. They provide that the testimony shall be taken in open court before a judge; they provide that the testimony shall be taken in shorthand, and a very important case can be finished in nineteen working days and even less; and if a Judge is not overwhelmed nor overburdened with work he can render a decision within a month thereafter. An excellent feature of the new rules is that upon petition the opposing experts will be required, within a certain number of days after the case has been put at issue, to file their expert opinions in the form of an affidavit, so that each side will have these affidavits before them as a basis for preparing for cross-examination of the expert witnesses in open court, and to enable them to see each other's positions, as far as these affidavits

will disclose them, in order to enable them to produce such fact witnesses as they may deem it necessary to produce to meet the attacks which the affidavits may indicate will arise. This, to a considerable extent, relieves the new practice from the surprises that may be sprung at the trial, and which, the nature of surprises in the expert side of the case would make it almost impossible for the opposing party to meet, since such matters frequently require experimentation. The affidavit of the complainant's expert witness, of course, is required to be put in first, and a certain number of days afterwards, that of defendant's expert. The cross-examination of the experts is conducted in open court.

My plaint is that we are suffering under the régime of a parsimonious republic. In the great Southern District of New York there are, at this writing, but four judges who are available for patent work: one of them has resigned, one of them is on leave in Europe, and the other two are staggering under a mass of litigation. Nor is it to be assumed by any means that a Federal Judge is a patent Judge only, for in one day I have heard motions on questions of immigration, bankruptcy, interstate business relations, injunctions in matters already decided, trademarks, copyrights, and patents; so that a Judge must needs be keen of eye and ear, clear of mind, and in the finest physical and mental condition possible to withstand the terrific onslaughts that are made upon what should be otherwise a man of mental equipoise.

In the parsimony of our republic the Attorney-General of the United States has decided that the vacancy which exists in this district shall not be filled with a new Judge, for the \$7500 meagre and insignificant salary can be saved if a Judge from some other district will occasionally come down and sit in the place of the one who resigned. In the meantime, infringements go on, injustice is meted out right and left, decisions cannot be had on cases pending on account of the overwhelming amount of work which crowds the dockets—all because our parsimonious, and,

<sup>1</sup> Presented at the 6th Semi-annual Meeting of the American Institute of Chemical Engineers, Troy, New York, June 17-20, 1914.

in this instance, peturious Government seeks to save a sum so insignificant in the business affairs of this Government, that it is hardly worth mentioning. If it were a real saving, nobody could criticize it, but it is not even a saving—it is a hardship, and has a destructive influence on the intellectual property of this country. I do not advise the building of one battleship less per year, but the building of only one battleship less for all time would give a fund sufficiently great to give us a new patent office building, which is so sorely needed, even though the money is at present available, and the interest on the balance at four per cent between the cost of this building and the cost of a battleship and its equipment, and the saving in the cost of maintenance of such a battleship, would give us fifty more Judges throughout the United States at a decent living wage, and place this country in the position that it should have been placed in years and years ago.

It is absurd that the United States Government should issue a patent for a consideration after making its usual objections and a more or less thorough search, and then repudiate its own action; but after spending a fortune and getting a decision it will cover only ONE circuit in the United States. Even the man who has recovered a decision on appeal could only sing, "*One-ninth of my country 'tis of thee, sweet land of liberty,*" for such a man stands in danger of having a Judge in another circuit overthrow what was done in the one; and where the philosophy, the justice, the reason, the sense and the equity come in, I fail to see, for if the United States Government is a sponsor for a patent it should be a sponsor for the entire United States, for it was so incorporated in the bond that was made between the fathers of this country and the people who sought their freedom and independence that each man shall have the right to pursue in peace his trade, and the exclusive right for a limited time shall be given to every inventor.

All that inventors want is the same protection that is given to real property or other personal property. If you buy a piece of real property in the United States, a search is made and title passed, and once you have it it is almost impossible for any one to deprive you of your ownership. In the purchase of other personal property the title is implied, for you are accustomed to buy from reputable people, and only in the case of stolen goods can the dispute of ownership be had; but when a man makes a new and useful invention it costs him almost all that he has to prove that the invention is his, and even after he has proved it he cannot collect damages excepting by due process of law. Let us hope that within a reasonable time the ownership of a patent will be the equivalent to the ownership of real property or other personal property.

It is puerile for any one to say the whole trouble with the patent situation today is the fault of President Wilson or Mr. Oldfield, or ex-President Taft. As a matter of fact, it is no one man's fault. Ex-President Taft sat in judgment on many a patent case when he was a Supreme Court Judge of the State of Ohio, and he, better than any one else, was aware of the shortcomings of the patent situation; and under his administration I believe it was largely by reason of his personal interest and experience on the bench, that the new equity rules were promulgated. Inasmuch as this is not a one-man Government it is not within the province of any one to make any personal criticisms. It is as much your fault as it is mine. What we are trying to do is to amend the situation by showing up the weaknesses that exist.

In closing, I recognize that my mail for the present is, more Judges. Some other battle-scarred veteran of the patent court wants the German system of six months publicity; a third man wants a Patent Commission; and so it goes on, but let me say that if every one of us had his wish, and that were the only improvement and remedy for the present, it would help a

great deal, but just as long as the Constitution provides that Congress shall make these laws so long will our voices fall on the desert air.

320 FIFTH AVENUE, NEW YORK

## SOME ECONOMIC ASPECTS OF INDUSTRIAL CHEMISTRY<sup>1</sup>

By BERNHARD C. HESSE

In considering this subject the difficulty lies not in a scarcity of material, but principally in keeping the discussion of the voluminous matter within a small compass.

The expression "industrial chemistry" has no universally accepted meaning and the reason seems to lie in the fact that, while a process may be essentially dependent upon a chemical reaction, yet the proportion of attention given or required of the chemist is small when compared with the other details of manufacture and control. For example, metallurgical operations require a chemical change in the ore before it yields the metal in its commercial form, yet few, if any, consider metallurgy a branch of industrial chemistry. It forms a distinct subject by itself, most likely because the mechanical and engineering requirements and details absorb more attention than the chemicals which have been worked out to what may be considered for our purposes as their final form, while the handling of material and the other mechanical problems call for constant supervision and scrutiny.

### INDUSTRIAL CHEMISTRY IN THE U. S. CENSUS

Taking the thirteenth census of the United States as a guide in ascertaining what is regarded by the Census as industrial chemistry, it will be found that in the division of chemical and allied products, metals and all metallurgical operations are excluded, as well as the production of refined petroleum, and a host of other large industries such as glass, soap, pottery, sugar, starch and the fermentation industries which depend upon chemical reactions and chemical control for their successful execution.

The Census of the United States includes under chemicals and allied products nine principal divisions:

- |                           |   |
|---------------------------|---|
| 1—Paint and varnish.      | 6—Sulfuric, nitric and mixed acids.                       |
| 2—Chemicals.              | 7—Wood distillation (not including rosin and turpentine). |
| 3—Fertilizers.            | 8—Essential oils.   |
| 4—Explosives.             | 9—Bone, carbon and lampblack.                             |
| 5—Dyestuffs and extracts. |   |

For the present, these nine divisions of the Census will be considered. Having arrived at a tentative conclusion as to the scope of the subject matter, this subject matter will be considered from the two following aspects:

I—The relationship of these industries to the manufacturing industry of the United States as a whole.

II—The position of the United States in those respects as a buying and selling nation.

The volume and distribution of foreign trade of the United States in the fiscal year of 1913 is given by the Department of Commerce as follows:

Exports.....	\$2,428,506,358
Imports.....	1,812,978,234
Total.....	4,241,484,592
Excess of exports.....	615,528,124

In order to obtain a conception of the relationship of these nine branches of chemical industry to the manufacturing industries of the United States as a whole, Table I will be helpful.

The story told by Column D is encouraging in some respects, and is not so encouraging in others. Compared with other manufacturing industries, the chemical and allied industries do not so easily lend themselves to small units. It takes 3.3 times as much capital for the average chemical plant as for the average manufacturing plant. This is the discouraging feature from the individual point of view.

<sup>1</sup> Lecture delivered at the College of the City of New York, May 1, 1914.



TABLE I—COMPARISON OF CHEMICAL AND GENERAL MANUFACTURING IN CONTINENTAL U. S.  
Manufacturing industries

Items	A	B	C	D(a)	E(b)
	Total	Chemical and allied products	Percentage of A in B	Average chem. plant, Av. general manuf. plant	Average in chemical plants for \$1 investment
1 Number of establishments.....	268,491	2,140	0.79	1.44	0.30
2 Persons engaged in manufactures.....	7,678,578	88,097	1.15	1.44	0.44
3 Proprietors and firm members.....	273,265	1,155	0.42	0.53	0.16
4 Salaried employees.....	790,267	16,516	2.09	2.64	0.80
5 Wage earners (average No.).....	6,615,046	70,426	1.06	1.34	0.40
6 Primary horsepower.....	18,680,776	398,880	2.14	2.71	0.82
7 Capital.....	\$18,428,270,000	\$483,729,410	2.62	3.31	
8 Expenses.....	18,453,080,000	359,425,126	1.95	2.46	0.74
9 Services.....	4,365,613,000	62,700,767	1.44	1.82	0.55
10 Salaries.....	938,575,000	24,042,566	2.56	3.24	0.98
11 Wages.....	3,427,038,000	38,658,291	1.13	1.43	0.43
12 Materials.....	12,141,791,000	258,115,975	2.13	2.69	0.81
13 Miscellaneous.....	1,945,676,000	38,608,384	1.98	2.51	0.76
14 Value of products.....	20,672,052,000	425,084,340	2.06	2.61	0.79
15 Value added by manufacture (value of products less cost of materials).....	8,530,261,000	166,968,565	1.96	2.48	0.75

(a) Values obtained by dividing separate items in C by Item 1 in C.

(b) Values obtained by dividing separate items in C by Item 7 in C.

From the broader point of view, Column D, however, is very encouraging. The average chemical plant requires 50 per cent more help than the average manufacturing plant; it employs over two and a half times as many salaried employees as does the average manufacturing plant, but unfortunately only 34 per cent more than the average number of wage-earners. The average chemical plant bears much more than its proportionate share of expenses, whether in the shape of salaries, wages, ma-

invested in chemical industry, it will be found on inspecting Column E that a dollar is not so productive in the chemical and allied industries, average against average, as in the other branches of manufacturing endeavor. The disbursements for salaries, materials, power, value of product and expenses of miscellaneous nature are each about three-quarters of the average of the same items for the other branches of manufacture, and the enhancement in value is only 75 per cent of the average enhancement

TABLE II—ANALYSIS OF CHEMICAL AND ALLIED PRODUCTS BY DIVISIONS

	VALUE IN DOLLARS	PERCENTAGE OF TOTAL DIVISION		VALUE IN DOLLARS	PERCENTAGE OF TOTAL DIVISION
PAINT AND VARNISH INDUSTRY			DYE STUFFS AND EXTRACTS		
Pigments.....	16,985,588	13.6	Artificial dyestuffs.....	3,462,436	21.6
Paints in oil.....	56,763,296	45.4	Extracts for dyeing.....	991,974	6.2
Yacutishes and Japans.....	31,262,535	25.0	Extracts for tanning.....	6,440,105	40.4
Fillers.....	3,126,271	2.5	Other tanning materials.....	625,401	4.0
Water paints and kalsomine.....	1,979,007	1.6	Mordants.....	99,797	0.6
Lined oil.....	1,912,594	1.5	Sizes and finishes.....	2,418,652	15.0
Bleached shellac.....	578,650	0.5	Ground and chipped woods, etc.....	344,761	2.2
All other products.....	12,281,481	9.8	All other products.....	1,562,448	9.7
Total.....	124,889,422		Total.....	15,954,574	
CHEMICALS			SULFURIC, NITRIC AND MIXED ACIDS		
Acids.....	11,926,389	10.1	Sulfuric acid.....	5,629,496	57.0
Sodas.....	21,417,982	18.1	Nitric acid.....	499,303	5.1
Potashes.....	38,940	0.7	Mixed acid.....	1,438,475	14.6
Alums.....	2,578,842	2.2	All other products.....	2,316,783	23.5
Coal tar products.....	2,675,327	2.3			
Cyanides.....	1,941,893	1.6			
Bleaching material.....	1,635,046	1.4	Total.....	9,884,057	
Chemical products made by the aid of electricity.....	17,968,277	15.2	WOOD DISTILLATION (not including rosin and turpentine)		
Plastics.....	7,180,172	6.1	Crude alcohol.....		
Compressed and liquefied gases.....	4,969,805	4.2	Refined.....	1,627,878	16.7
Fine chemicals.....	10,956,666	9.3	Acetate of lime.....	2,901,709	29.8
Chemicals not elsewhere specified.....	34,349,548	29.1	Charcoal.....	1,981,220	20.3
Total.....	117,688,422		Turpentine.....	2,351,644	24.0
FERTILIZERS			All other wood distillation products.....	249,526	2.6
Fertilizers.....	92,369,631	88.8	All other products.....	357,290	3.7
Superphosphates.....	15,318,529	(12.8)		2,677,731	2.8
Ammoniated fertilizers.....	10,061,193	(9.7)	Total.....	9,736,998	
Concentrated phosphate fertilizers.....	3,638,210	(3.5)	BONE, CARBON AND LAMPBLACK		
Complete fertilizers.....	57,243,899	(55.0)	Bone black.....	1,070,333	50.0
Other fertilizers.....	8,107,800	(7.8)	Carbon black.....	625,514	29.7
Sulfuric acid for sale (as 50° Bé acid).....	923,492	0.9	Lampblack.....	439,707	20.6
Other acids for sale.....	611,288	0.6	Total.....	2,135,554	
All other products.....	10,055,802	9.7	ESSENTIAL OILS		
Total.....	103,960,213		Oil, peppermint.....	519,079	29.8
EXPLOSIVES			Oil, black birch.....	102,045	5.9
Dynamite.....	18,699,746	46.6	Oil, spearmint.....	83,283	4.8
Permissible explosives.....	863,209	2.2	Oil, wintergreen.....	68,983	3.9
Nitroglycerin.....	3,162,434	7.9	Other oils.....	335,213	19.3
Explosive powder.....	9,608,226	24.9	Witch-hazel extract.....	412,322	23.7
Gunpowder.....	1,736,427	4.3	All other products.....	216,309	12.4
Other explosives.....	3,913,787	9.7	Total.....	1,737,234	
Materials not elsewhere specified.....	2,155,793	5.4			
Total.....	40,139,661				

terials, or miscellaneous expenditures; in the value of the product produced per unit of chemical plant the average chemical plant produces 161 per cent more than its average share.

If the principal object of manufacture be the enhancement of value of the outgoing material over the incoming material, then the fact that the average chemical plant enhances its raw material 148 per cent more than its average share is a matter for congratulation and of encouragement.

Turning now to the question of productive power of capital

produced by unit capital investment in the other branches of manufacture. The dollar so invested employs fewer wage earners, salaried or otherwise, than a dollar otherwise invested in manufacturing enterprise. This, of course, is merely a natural consequence of the high initial cost of plant, the large size of plant required and the close markets.

Turning to the value of products in Column B, it is to be noted that the percentage participation of each of the nine divisions in that title is as follows:

Paint and varnish.....	29.4	Sulfuric, nitric and mixed	
Chemicals.....	27.4	acids.....	2.3
Fertilizers.....	24.5	Wood distillation.....	2.3
Explosives.....	9.4	Essential oils.....	0.3
Dye-stuffs and extracts.....	1.8	Bone, carbon and lampblack	0.4

The thirteenth census of the United States has distributed the participation of these nine divisions in this amount of product with considerable detail, which does not lend itself very well to discussion. The not specifically described items amount to \$73,563,059 or 17 per cent of the total. For the purpose of obtaining a better understanding of the relationship of the various principal items under each of these nine divisions, Table II has been prepared.

Within the nine divisions given, the United States is in a large measure self-sustaining, although it is necessary for it to obtain much of the raw material from abroad. In the division of dyestuffs and extracts, and particularly that portion of it dealing with artificial dyestuffs, it is to be noted that during 1913, the total importation into the United States of artificial dyestuffs, exclusive of alizarine dyes and indigo, amounted to \$7,105,284; during the census year of 1910, this country manufactured \$3,462,436 worth of such artificial dyestuffs which amounts roughly to 32 per cent of this country's entire consumption of the so-called coal-tar dyes; no doubt, since the census year 1910, the domestic production of coal-tar dyes has increased. However, much of the coal-tar raw material used in such manufacture comes to us from abroad, particularly from Germany and England.

In the fertilizer division we are, of course, dependent, for our potash requirements, upon Germany, and these amount in round numbers to \$1,000,000 per month. In the same division, we are dependent upon Europe for much of the ammonia entering into the fertilizers, amounting in 1910 to over \$4,000,000. It will probably not be long before most of our ammonia requirement is supplied by our own by-product coke-ovens.

#### INDUSTRIAL CHEMISTRY IN ITS BROAD ASPECT

However, industrial chemistry or chemical industry is much broader in scope than is indicated in the thirteenth Census of the United States on chemicals and allied products. From the point of view of the person with chemical training, every industrial operation which calls for chemical control is a branch of industrial chemistry or of chemical industry, the two terms being used interchangeably.

In Germany the official classification of material connected with chemical industry is as follows:

- 1—Malt, oil fruits, plants, etc.
- 2—Industrial or medicinal vegetable products.
- 3—Tanning extracts.
- 4—Resins, gums and adhesives.
- 5—Caoutchouc and camphor.
- 6—Animal and vegetable fats and oils.
- 7—Animal products.
- 8—Starch and sugar.
- 9—Alcohol, acetic acid, mineral waters.
- 10—Mineral and fossil raw materials.
- 11—Ores, iron and slags.
- 12—Fossil fuels.
- 13—Mineral oils and like fossil raw materials.
- 14—Coal-tar oils and products.
- 15—Waxes.
- 16—Soap and fat products.
- 17—Chemical and pharmaceutical products.
- 18—Miscellaneous chemical and pharmaceutical products.
- 19—Dyes and dye materials.
- 20—Ethers and alcohols.
- 21—Volatile oils, synthetic perfumes, toilet articles.
- 22—Artificial fertilizers.
- 23—Explosives and combustibles.
- 24—Wood fiber and chemical paper.
- 25—Metals.

These twenty-five large classes or divisions comprise four hundred and forty-two sub-classes.

An examination of the records of imports and exports into and from the United States during the fiscal year 1913, discloses a total business of \$4,241,484,592; of this, not less than \$1,302,274,994 or 30 per cent deal with products of chemical industry or materials used in the products of chemical industry, and of these \$759,193,688, or 18 per cent of the total represent imports and \$543,081,306, or 12 per cent of the total represent exports, leaving a balance of trade against the United States, \$216,112,382.

#### LARGE ITEMS IN CHEMICAL TRADE OF THE U. S. FOR 1913

IMPORTS		EXPORTS	
Sugar.....	\$204,212,581	Refined petroleum and its products...	\$139,882,995
Hides and skins.....	117,386,174	Copper as metal.....	120,605,914
Unmanufactured India rubber.....	101,333,158	Beef and hog products.....	82,890,777
Paper and paperstock.....	27,706,697	Leather.....	42,384,199
Potash compounds.....	14,408,124	Naval stores.....	26,471,492
		Fertilizer material.....	11,400,888
		Cement industry.....	5,822,105
	\$465,046,734		\$429,458,282

Information as to the distribution of the exports and imports just given as to countries of destination and countries of origin is not readily accessible, since it would be a never ending task for the officials of the Department of Commerce to rearrange all of this vast information from the various points of view possible.

#### MOVEMENT OF CHEMICAL PRODUCTS BETWEEN GERMANY AND THE UNITED STATES

However, fragmentary information is accessible with respect to the relationship between the United States and Germany as regards the interchange of chemical products between the two countries. This information is based upon German official publications.

From the point of view of values, information<sup>1</sup> is at hand for only the year 1904. In that year Germany sent to the United States \$16,993,200 worth, and the United States sent to Germany during that time \$38,194,240, or an excess in favor of the United States of \$21,201,040, which means about \$1,800,000 per month.

With regard to the tonnage movement between those two countries, information for the year 1913 is at hand,<sup>2</sup> and it shows that during that period a total of 3,430,564 metric tons of commodities of the chemical industry passed between the two countries, of which 1,917,430 metric tons passed from the United States to Germany, and 1,513,134 metric tons passed from Germany into the United States; that is, the United States sent to Germany an excess of 404,000 tons over what it took from Germany in 1913.

#### FREIGHT MOVEMENTS IN THE UNITED STATES

In 1911 the total freight movement over the railroads of the United States amounted to 967,233,991 tons; of these about 14 per cent comprised manufactured goods, and about 28,000,000 tons of the total freight moved was composed of products of chemical industry, that is, about 3 per cent of the total freight movement of this country is represented by products of chemical industry. The three and a half million tons gross above referred to between the United States and Germany, therefore, represent about 12 per cent of the probable total freight movement of products of chemical industry in this country.

#### EFFICIENCY OF AMERICAN INDUSTRIAL CHEMISTRY

An examination of the relative exports and imports of products of chemical industry from and into the United States shows that there is little, if any, ground for criticism of American chemists in not utilizing their opportunities. It is safe to say that the American chemical industry is developing its own natural resources with a degree of foresight and success very favorably

<sup>1</sup> THIS JOURNAL, 6, 2

<sup>2</sup> Ibid., 6, 274.

comparable with that accomplished by chemists in other lands. Much is heard in criticism of American chemists for not developing a coal-tar chemical industry, but I do not believe such criticism to warrant a wholesale belief in the backwardness of American chemists. There can be no question that the chemical work involved as well as the engineering work involved in the production of a useful and usable illuminating oil, or a medicinal preparation from crude petroleum, compares very favorably with the chemistry involved and the engineering involved, in the production of the majority of so-called coal-tar dyes. The relative economic value of the two products is, of course, in favor of the products of petroleum. It will be sufficient to say Germany is supreme in the coal-tar dye industry, because (1) Germany was the home of the industry; (2) the industry itself is so dependent upon interlocking chemicals and the growth of this interlocking dependence has been as fast as economic development warrants and has now reached such a stage of complexity and interdependence that it is difficult of transplantation as a whole; (3) there are relatively few so-called staple articles among the coal-tar dyes—by staple is meant those which are consumed in quantities to be measured by tons—many of those few are so interlocked with subsidiary or by-products that the transplantation of the work out of Germany would be economically unprofitable. Wherever it has been profitably transplantable to this country, the manufacturing of such staples has been done, and with considerable success even though the raw material supply is still provided by Europe.

#### THEORY AND PRACTICE

The chemical industry, probably more than any other industry, is dependent upon the application of much theoretical work, *i. e.*, scientific work to every-day conditions, and in order that the chemical industry may grow, it is necessary that there should be brought to bear upon the manufacture of each and all of the products the highest chemical training available under the circumstances. The beneficial interaction of practice upon theory and theory upon practice, is evident in almost every branch of industrial chemistry. It has been brought to its highest efficiency, however, in the organic division, and more particularly that dealing with coal-tar dyes and synthetic medicinals and pharmaceuticals. However, the chemist can, with profit, follow Mr. Kerr's excellent advice to engineers when a difficulty is encountered: "Go as far as you can see and then see how far you can go."

The simplification brought about in organic chemistry through the creation of the Kekulé conception of the structure of benzol, made the development of the coal-tar dye industry in its early stages possible, or at any rate immeasurably facilitated it. In return, the coal-tar dye industry has enriched scientific or theoretical organic chemistry with a wealth of information and facts with respect, not only to benzol, but to naphthalene, anthracene and the higher aromatic hydrocarbons; the two working together have developed a very large number of new classes of organic compounds, for example: the azines, oxazines, numerous classes of azo compounds, and the wealth of oxy and oxamido derivatives in all the classes. New methods of sulfonation, chlorination and nitration have been developed almost without number, and in turn, theoretical organic chemistry has supplied the industry with many useful methods of the same kind.

To contemplate the results of this interaction is to view one of the greatest of intellectual triumphs. It is this very fact that has misled so many to ascribe to the coal-tar dye industry an economic effect far beyond its actual and to belittle the economic effect of the so-called inorganic industry. It is perfectly safe to say that the money value of the inorganic exceeds the money value of the dye industry by at least 15 to 1.

From 1877 down to the close of 1912 there were taken out in Germany 5,675 German patents, or 158 per year, dealing with the utilization of coal-tar hydrocarbons and their by-products;

it has been estimated that not more than one out of every hundred has secured financial returns for its owners. During the years 1895 to 1903, 382 German patents, or at the rate of 48 per year, were taken out in the inorganic chemical industries.

It would be an interesting subject for speculation to consider the intellectual effort involved in the 5,675 coal-tar patents as compared with the intellectual effort required for the 382 inorganic patents. It would also be of interest to consider the difficulties, financial and otherwise, in the way of creating those respective patents. A far-reaching experiment can be made in the coal-tar industry for a very little expenditure of material and labor, but in the inorganic industry the expenditure of material and labor is inordinately greater. You can make a coal-tar dyestuff and determine whether there are any probabilities of its having commercial utility at an infinitely slighter expense than you can determine whether certain alterations in the construction of a bleach-chamber in the production of bleaching powder will or will not be profitable; on the other hand, as you approach the more highly developed and almost completed manufacturing phase of coal-tar dye chemistry, you immediately come into about the same difficulties and embarrassments that you do in the inorganic field, and for precisely the same reason, namely, that in both cases you are endeavoring to develop refinements, and refinements are much more difficult of detection, elaboration and application than is the question of determining whether you have, or have not, a new and probably useful dyestuff.

By way of illustration, there are probably fewer than 35,000 compounds listed in Beilstein, but it will be no difficulty whatever to find a dozen different patents on coal-tar dyes, each and every one of which covers several million, even several hundreds of millions of different and distinct dyestuffs. Of course, to discover a new type of a dyestuff is almost as difficult as it is to discover a refinement in the almost fully developed inorganic industry, but once the type is given, there is no difficulty in creating a new dyestuff under that type.

#### THE FUNCTION OF THE CHEMIST AS AN INDIVIDUAL

Now, the function of the chemist in the production of things is twofold. Take the apparently most humble position, namely, that of analyst. Upon his accuracy of manipulation depends, in a large measure, the profitableness of the undertaking. If an analyst makes a mistake of 1 per cent in determining copper, on the \$120,000,000 worth that we export annually, that would mean a loss of \$100,000 per month. Therefore, analytical control, in order to be of value, must be accurate, since inaccuracies can easily run into large sums of money.

But the chemist's contribution does not stop merely with control; he does create a great many new uses for old things, and he does create new things and find uses for them. To be able to do these things to the best advantage, he must be thoroughly versed in what has been done, must know what tools are at his command, must be able to use those tools and to tell when they shall be used, must possess also the merchant's instinct of values, if he desires to rise to the highest efficiency in industrial chemistry. Of course, he must know how to handle men, and how to get results with what is at his command, as must anyone who attempts to conduct any business enterprise.

He must be alert, and he must overcome any disdain that he may naturally have for small things, for in industrial chemistry, perhaps oftener than in any other, it is the small thing that has pointed the way to achievement and success.

It is an old story how the production of benzol from coal gas was brought about by a mistaken notion that oxalic acid could be made from coal gas and nitric acid. An alert and very observant chemist in repeating this attempted synthesis found not only that oxalic acid was not formed, but that nitrobenzol was produced with benzol dissolved therein. That was the beginning of the recovery of benzol from coal gas, and the ad-



dition to the sources of benzol of a source much greater and more dependable than any theretofore available.

The neglect of a laboratory boy to maintain the temperature he was directed to keep in a certain vessel, taught that laboratory boy nothing, but the chemist in charge following up this result, finally ended up with a method of substituting sulfuric acid for bromine, thereby reducing the cost of production by over 50 per cent. In both of these cases, it is very doubtful if a man having no training beyond that required in the production of the things with which he was directly concerned, would ever have made those discoveries. The attempt to make oxalic acid would have resulted in failure, and would have been so reported, the result of the laboratory boy's negligence would have been dumped into the sewer, and a new start made along the original lines.

#### CONCLUSION

I have shown how, in a national sense, the chemical industry contributes a very substantial portion to our national welfare and the useful part it plays in this work-a-day world, in the employment of persons, materials and of capital; how in a broader sense it touches almost every field of human activity; how it is interwoven with the means required for the gratification of all our personal needs and desires.

It needs merely to be mentioned in order to bring about a full appreciation of the importance of the chemical industry to refer to the important part it plays with respect to agricultural chemistry. The chemical methods of investigation and research applied to agricultural problems indicate the requirement of certain materials by the soil, and these materials are supplied by the chemical industry. In that way the chemical industry contributes to the activity of the soil and the increased output per unit area of agricultural products.

Conversely, as in the case of alizarin and indigo, hundreds upon hundreds of square miles of the earth's surface were devoted to the cultivation of the plants necessary to produce these articles. This very large area is no longer required for that purpose, and it is safe to say that in the chemical factories now producing these things the combined working area is under four square miles. Right or wrong, I have always personally felt that had the botanist devoted the necessary attention to the growth and cultivation of indigo plant when the first synthesis of indigo was announced in 1880, the displacement of vegetable indigo between 1897 and 1900 by synthetic indigo would not have taken place, or at any rate, it would not have been accomplished after so brief a struggle. The botanist has assisted wonderfully in increasing the alkaloidal content of cinchona barks, and in the discovery of a large number of new plants capable of producing a latex suitable for India rubber production and he has also contributed greatly to the development of plantations, wherein the yield per unit area is much increased.

While at the present day it may not be commercially profitable to produce synthetic rubber, or synthetic camphor, or synthetic nitric acid, or synthetic ammonia, yet it is perfectly true that the very existence of these possible synthetic sources of these materials renders it less and less likely that there will be any undue advance in the cost to the consumer of these articles; at any rate, the cost will not be advanced beyond a figure where the synthetic process can achieve a reasonable profit.

Chemical industry, therefore, not only provides for our present needs, but acts as safety device against famine, shortage or undue monopolization of a number of vegetable and mineral products.

90 WILLIAM ST., NEW YORK

#### CHEMICAL STUDIES OF THE POLLUTION OF THE OHIO RIVER<sup>1</sup>

By EARLE B. PHELPS

The extensive investigation of the Ohio river now being under-

<sup>1</sup> Presented at the 49th Meeting of the American Chemical Society, Cincinnati, April 6-10, 1914.

taken by the U. S. Public Health Service under the direction of Passed Assistant Surgeon Wade H. Prost has a twofold object. It is desired to learn primarily the extent and character of the pollution now entering the Ohio river, the capacity of that river to receive and dispose of pollution, and the effect of such pollution upon the waters of the river and upon the health and comfort of the riparian dwellers. Secondly, and possibly of equal ultimate importance, it is hoped to establish certain basic data necessary to a general discussion of the principles of the self-purification of streams.

No such comprehensive investigation of a great river system has ever been made. In addition to chemical, biological and bacteriological, and hydrographic studies of the river itself and of the polluting waters, the investigation will include sanitary surveys and epidemiological studies of the bordering communities and engineering studies of water supplies and sewerage systems.

River pollution may be regarded from the point of view of the river itself or of the health of the people dwelling upon its banks. The sanitary qualities of a drinking water, and the effect of pollution upon riparian dwellers is essentially a biological question to be studied by biological methods, supplemented at times by chemical methods. The question of nuisance in a stream, although it deals with biological agencies, is essentially chemical and necessitates chemical or biochemical studies.

The present paper deals solely with the chemical part of this investigation, as applied to the pollution and self-purification of the stream. It will be pertinent, therefore, to present first, a general statement of the problem as it appears in the light of modern sanitary chemistry.

The self-purification of streams is in no way a unique or remarkable process. It is essentially like the oxidation and destruction of organic matter by the soil. In the case of a polluted stream, however, purification by oxidation is assisted by other factors, such as dilution and sedimentation, which together with the ideal conditions for oxidation which may exist, combine to produce such improvement that the phenomenon has ever been regarded as one peculiar to itself.

The reactions involved in this process are biochemical reactions. For their occurrence it is necessary to bring together oxidizable organic matter, oxygen and oxidizing bacteria. The first and last are necessarily present in polluted waters. The questions of stream purification and prevention of nuisance, therefore, reduce to one of oxygen supply.

The ultimate source of the oxygen available for this work is the atmosphere. Under normal atmospheric conditions and at any given temperature, water dissolves a specified quantity of oxygen which, unfortunately, is known as the saturation value. This incorrect usage has resulted in serious misconceptions of the true solubility relations of oxygen. Since the solubility of any gas is proportional to the partial pressure of that gas in the atmosphere above, it follows that the solubility of oxygen in water is approximately five times as great under an atmosphere of pure oxygen as it is under a normal atmosphere. Hence "supersaturation" is readily obtainable. It is of frequent occurrence in nature in the neighborhood of green plant life where the oxygen content of the immediate atmosphere, or of the gases rising through the water, is greater than in the normal atmosphere. It would be eminently desirable to refer the solubility of oxygen to a pure oxygen atmosphere in which case the accepted saturation value would be reduced to approximately 20 per cent; but usage has sanctioned the present method which makes it necessary for us to deal with "supersaturation."

A saturated water will obviously dissolve no more oxygen. Atmospheric oxygen tends to re-enter the water in proportion as the oxygen content of the water is lowered by the oxidation of organic matter. The intensity of the driving force of re-

aeration is a direct function of the lowering of this oxygen content. It is at a maximum in a completely deoxygenated water and this is the condition of maximum oxidizing work in any stream. This condition, however, is also one of maximum nuisance and is not to be tolerated. Such an anaerobic stream gives off foul odors and is black and unsightly in appearance.

It becomes a matter of some importance, therefore, to determine the minimum value which the dissolved oxygen of the stream may reach before conditions approach the nuisance stage. This point practically fixes the capacity of the stream in question to care for pollution. The lower the permissible oxygen concentration the greater the proportion of the initial dissolved oxygen of the water available for the oxidizing reaction, and the greater the capacity of the stream to reabsorb oxygen from the atmosphere.

Upon this question of permissible oxygen reduction there are many diverse opinions and very little real knowledge. It has even been held that any oxygen whatever will prevent conditions of serious nuisance. The present writer's experience has not tended to confirm this view. That condition of nuisance, for example, which makes a river undesirable for canoeing on a quiet summer evening by reason of sewage odors emanating therefrom has been found to result from a reduction to fifty per cent of saturation. Extremely offensive conditions, with foul odors and black appearance, have been found to be associated with 38 per cent of saturation. On the other hand certain streams which have ranged from 60 to 75 per cent of saturation have given to the senses no direct evidences of pollution. This point needs further study and discussion. It is merely desired to draw attention at this time to its importance as one of the fundamental factors of the problem.

The second and most important factor is the re-aeration. The rate of re-aeration of water depends not only upon the oxygen concentration existing at the time but upon the vertical distribution of that concentration. Assume, for example, that the water is uniformly mixed and quiescent. Absorption at the surface leads to a downward diffusion which in time establishes a gradient ranging from essential saturation in the upper film to the initial concentration at some point below. The diffusion process becomes slower as the curve of distribution of oxygen becomes flatter. In practice, quiescent water, even though it start with zero oxygen concentration at all points, will, except in shallow layers, come to a condition of practical equilibrium with very low average oxygen concentration. Beyond this point the diffusion process is so exceedingly slow as to be quite negligible. Mixing of the water, after such a condition has become established, reestablishes the even distribution and allows the absorption to proceed toward a new condition of equilibrium. It is apparent, therefore, that, as conditions depart more and more from the condition of complete quiescence, the rate of re-aeration is increased accordingly. The departures from quiescence may be definitely stated, and are more easily conceived, as the average time between uniform mixings. This form of expression is used, not only because it gives a workable statement of the degree of agitation in a stream, but because such a time factor appears in any formula for re-aeration derived from the laws of solubility and of diffusion. Such a formula was developed by William M. Black, Colonel, Corps of Engineers, U. S. A., and the writer in an investigation of the pollution of New York Harbor.<sup>1</sup> In that case it was possible to determine the average time between mixings from a study of the mixing effect of winds, vessels and tidal currents. The re-aeration calculated from this theoretical formula, using the determined time factors, was in close agreement with the actual values found during the subsequent year and thus gave satisfactory confirmation of the accuracy of the method. With the deep and rela-

tively quiescent waters of New York harbor re-aeration was found to be almost a negligible factor. The capacity of such a body of water to oxidize pollution is practically limited by the amount of available oxygen brought in from the ocean with each tide.

Under river conditions matters are directly reversed. The initial volume of available oxygen is small compared with the total capacity of the stream to oxidize pollution. Re-aeration in rivers is the chief factor. The time between mixings, instead of being measured in hours, is probably measured in minutes, so that its actual determination from direct observations cannot be made with even workable precision. It becomes necessary, therefore, to reverse our process of reasoning, to learn by suitable methods the actual extent of re-aeration, and, from those data, to derive the time factor in the original aeration formula. This factor will vary with the depth, character of the river bed, and rapidity of flow. It will differ, therefore, for various rivers and for various sections of each river but should be similar for similar types of stream. If it can be determined for a sufficiently large number of typical stream stretches, it may be possible to deduce general formulas which will be applicable to other streams of similar type. This, then, is the second important factor to be investigated in our stream studies and if it can be satisfactorily determined it should be possible to estimate the capacity of a given river to dispose of pollution without objectionable results, or, conversely, the effect of any stated pollution upon a river of given type.

The actual rate of re-aeration in a polluted stream cannot, unfortunately, be determined directly. In spite of re-aeration a stream at any given point may be losing oxygen, or it may be in oxygen equilibrium, since at all times the biochemical reaction tending to reduce the oxygen is opposed to the actual re-aeration. It is necessary therefore to develop suitable chemical methods for the separation of these opposing tendencies.

Consider first an ideal situation with two sampling stations on the stream between which stations there is no increment either to the pollution or to the volume of the stream. These conditions cannot, as a rule, be obtained and it is necessary to make suitable correction for the interference of additional pollution or additional dilution. The oxidizing reaction has been studied in the laboratory sufficiently to show that it follows a fairly definite course and like all biochemical reactions is essentially monomolecular in its order. This means that it proceeds at a constant rate or velocity so that the concentration of oxidizable material decreases as a logarithmic function of the time. A sample of the water from the upper station is submitted to study for the determination of three things: (1) The available oxygen which it contains; (2) the total amount of oxygen which will be required for the completion of the oxidizing reaction, known as the oxygen demand; (3) and the velocity with which that reaction proceeds. The sample from the lower station is submitted to the same examination. Since any loss of available oxygen by oxidation must give rise to an equivalent loss in the oxygen demand, the difference of these two terms would remain constant throughout the course of the reaction, in the absence of re-aeration. Any increase in dissolved oxygen at the lower station over the value calculated from the results of examinations at the upper station is therefore due to aeration. Correction for additional pollution or dilution between the stations is next made by means of the velocity of reaction determinations. From the determination at the upper station and the known time required for water to pass from one station to the other, the concentration of reacting substance at the lower station is calculated. With increasing dilution the concentration is decreased, while with increasing pollution it is increased. Any change in the concentration, calculated from an assumed constant velocity of reaction indicates an equivalent change in dilution or pollution between these stations. It is obvious that

<sup>1</sup> Report of Colonel William M. Black, U. S. A., and Earle B. Phelps, on the "Discharge of Sewage into New York Harbor," March, 1911.



these two factors are opposed to one another in a plus and minus sense and that if the added water were of the same character relative to its pollution as the water under investigation, the correction factor would disappear. In brief, from the known constant velocity of reaction, stated in terms of physical chemistry, are determined changes in the concentration of the reacting substance, namely, pollution.

The actual laboratory technique of these determinations is simple. The usual dissolved oxygen determinations are made upon a freshly collected sample; a second sample is incubated at 20° C. and a dissolved oxygen determination made upon it at the end of any convenient period, usually 24 or 48 hours. The difference between these two results is the oxidation that has taken place in the interval. Knowing the form of the reaction curve one computes from this, first, the velocity coefficient of the reaction and then, by extrapolation to a very long time, the total oxygen demand of the polluting organic matter. These two determinations at each station furnish the required data, but there are many points that require special attention. It is necessary in the first place to secure an adequate sample of the entire cross section of the stream. This involves the careful selection of sample stations and the sampling of a stream at various points in the cross section both vertically and horizontally. It is desirable in the second place to select stretches involving a minimum correction for additional pollution or dilution and it is quite necessary finally to consider the effect of sedimentation. This can be arrived at only by a study of the surface of the river bottom. A special apparatus is necessary for the withdrawal of the surface deposit from a given area of bottom and it is necessary to make a careful survey of the river bottom between stations from time to time. A new reaction velocity must be determined for this deposited material and suitable correction made to the average findings in the water above for the period between the two bottom mud surveys. Finally the temperature of the river is not that at which the incubations are made. The temperature coefficient of the reaction must be known and suitable correction applied.

It will perhaps be noticed that no attention has been given in the foregoing discussion to the supposed relation between concentration of sewage in water and probable nuisance. This factor has heretofore been the chief theme in any discussion of stream pollution and self-purification. Recognized authorities have variously estimated stream flows of from 2.5 to 3.5 cubic feet per second per thousand persons contributing, as the danger line. A still less correct statement is often made in that sewage dilutions of from 1 in 16 to 1 in 23 will undoubtedly produce nuisance. A little consideration of the true factors of self-purification will show that any such form of statement is entirely incompatible with the facts. A deep quiescent swimming pool may become putrescent even with the slight amount of organic pollution which it receives. A one per cent dilution of sewage in water will often putresce under laboratory conditions. Deep and slow-moving bodies of water such as are found in canals or in rivers behind dams, especially if they be protected against wind action, have very little capacity for re-aeration and are in consequence much more affected by sewage than rapidly running and relatively shallow streams. The maximum oxidizing work occurs under conditions of minimum depth and maximum agitation. Any discussion, therefore, of permissible concentration of sewage in water without reference to the character of the stream in question is futile and misleading.

It is proposed to study by the methods outlined the rate of re-aeration of the Ohio river at a great many points, but particularly below the three points of greatest pollution, namely, Pittsburg, Cincinnati and Louisville. In none of these cases are the conditions ideal and it will be necessary to do a large amount of work to obtain results of satisfactory precision. As an additional check upon results it is also proposed to make as thorough

a study as practicable of the actual polluting material entering the river at these three points. The total oxygen demand and the velocity of the oxidizing reaction will be determined upon this initial pollution in a manner similar to that which has been described. In case of concentrated organic matter, the methods are modified by first diluting in suitable proportions with aerated water. Further checks upon the work involve similar studies upon the tributaries and upon pollution from smaller communities between stations. Moreover, instead of the two stations which have been used in illustration, the work will actually comprise a chain of stations for regular study. In addition, connecting data will be obtained by means of house boat laboratories. The three regions of maximum pollution are fortunately of three distinct types. The river below Pittsburg is a series of short pools separated by shallow water flowage. Below Cincinnati there is a long quiescent stretch in which sedimentation will be an important factor. At Louisville there are rapids giving a minimum of sedimentation and a maximum of aeration. Certain special minor points such as the effect of low temperature upon aeration and the effect of long quiescent stretches upon sedimentation will also receive special study.

It is anticipated as a net result of this chemical portion of the Ohio river investigation that sanitarians will be in a position to discuss with much more assurance than at present the general principles which underlie the phenomenon of the self-purification of streams.

HYGIENIC LABORATORY  
U. S. PUBLIC HEALTH SERVICE  
WASHINGTON

## THE APPLICATION OF PHYSICAL CHEMISTRY TO INDUSTRIAL PROCESSES<sup>1</sup>

By WALTER F. RITTMAN

The luxury of today is the necessity of tomorrow; likewise the theory of today is the practice of tomorrow. Gayley's process of drying air for a steel furnace, the various nitrogen-from-air processes, the contact process of manufacturing sulfuric acid, synthetic indigo, synthetic tanning materials—all were in the field of abstract theory but a few years ago. Today they are practical realities. Similarly, many of the theoretical principles and processes of today will, in all probability, be realities a few years hence.

The invasion of chemistry by physics, and the production of what is known as physical chemistry, promises to be a most important basis for progress in the field of applied chemistry. Whereas physical chemistry is often looked upon as one of our most theoretical subjects, it will be found to be one of our most practical as well. Its principles are useful regardless of the materials involved in the reactions, whether copper, steel, soap, glass, cement, gas, textile, or any other chemical product. Physical chemistry is described as that branch of chemistry which has for its object the study of the laws governing chemical phenomena. When these laws and their application to a reaction or process are once understood it is a relatively easy matter to select the most favorable physical conditions. The task of the chemical engineer is to produce these most favorable working conditions in an apparatus which operates on an industrial scale. A further advantage of a knowledge of theoretical principles and perhaps one to be more frequently applied is the aid such knowledge gives in avoiding fantastic so-called improvements.

The chemical engineer rarely creates new products; he deals with processes and machinery which produce quantities economically. Obviously his problems often differ from those of the laboratory chemist. The fact that a reaction is slightly exothermic or endothermic is of secondary consequence in laboratory experiments, but in applied engineering this fact at once de-

<sup>1</sup> Presented at the 6th Semi-annual Meeting of the American Institute of Chemical Engineers, Troy, New York, June 17-20, 1914.



termines whether the reaction should be carried out in a cooled or in a heated apparatus. The amount of heat given off in a reaction, such as the hydrogenation of a vegetable oil, is of no serious consequence in laboratory experiments, but where tons are handled the accumulated heat is sufficient to ruin any process which does not provide for its disposal. Latent heat of fusion or of evaporation is not important in the laboratory where there is always an excess of heat or cold, but in many cases this heat of fusion or of evaporation becomes all important in its influence on the cost of an industrial operation. The cost of the heat absorbed by an endothermic reaction seldom concerns the laboratory chemist; but it is profit or loss to the chemical engineer. The percentage of yield, and the cost per unit, are the vital questions to the engineer; they are usually not vital to the laboratory chemist, however valuable and constructive his work may be.

It sometimes seems as if the inertia of years has limited the temperate imagination of many engineers and some chemists. Theoretical considerations might suggest the broad field which comprises the several thousand available degrees above the boiling point, as well as the 273 degrees below the freezing point of water. Likewise, we are prone to overlook the great advantages which sometimes may be derived from the application of pressures greater or less than the one atmosphere which surrounds us and with which we are so familiar.

Because of the numerous possibilities in the application of physical chemistry to industrial processes, I must greatly restrict myself in dealing with the subject. Some of the most interesting parts deal with equilibrium relationships, phase rule applications, radioactivity, energy considerations and electrolytic reactions. Excellent examples illustrating the successful application of each can be found, but today I shall deal in some detail only with the one mentioned first, *i. e.*, equilibrium relationships.

I shall not attempt to deal with every branch of modern production which involves the equilibrium relations of physical chemistry, nor shall I attempt to advance speculations as to future applications of equilibrium relations in industry. The attempt will be confined to successful present-day applications, by way of examples. However familiar these processes may be, I hope that there will be at least something interesting, if not new, in pointing out that these familiar processes have a purely theoretical aspect. In fact, dealing with them historically indicates that they have all developed out of the most abstract theoretical reasoning into the practical machinery of economical production.

#### OXIDATION OF NITROGEN FROM AIR

It is known that at room temperature there is no perceptible union of the nitrogen and oxygen of air; it is known that at temperatures as high as 3000° C. only a partial union takes place; it is known that the amount which does unite is a function of the temperature; that is, at each temperature there is a definite percentage of nitric oxide formed, and equilibrium exists between the combined and uncombined constituents. In other words, the tendency of the uncombined constituents to combine at any particular temperature is exactly counterbalanced by the tendency of the combined constituents to separate at that temperature. There is a true equilibrium. Experiment has proven that when air analyzing 79.1 per cent N<sub>2</sub> and 20.9 per cent O<sub>2</sub> is brought to equilibrium at 2400° C. the resultant mixture analyzes 2.23 per cent NO, 77.98 per cent N<sub>2</sub> and 19.78 per cent O<sub>2</sub>; *i. e.*, 1.116 per cent of an atmosphere each of nitrogen and oxygen have disappeared in the formation of nitric oxide. Further, let it be clear that this 2.23 per cent of NO obtained at 2400° C. is not an accidental figure; it will always be the same when air of the above composition is brought to equilibrium

at 2400° C. This fact makes it possible to calculate the equilibrium constant for nitrogen, oxygen and nitric oxide at 2400° C.

$$\text{N}_2 + \text{O}_2 \rightleftharpoons 2\text{NO} \quad 43,200 \text{ cal.}$$

$$K_{2400^\circ \text{C}} = \frac{p_{\text{NO}}^2}{p_{\text{N}_2} p_{\text{O}_2}} = \frac{(0.0223)^2}{(0.7798)(0.1978)} = 0.0032$$

where *p* represents the partial pressures of each of the three constituents; *i. e.*, the part of the whole pressure exerted by each. The constant *K* which joins these partial pressures has a definite numerical value for each definite temperature. The square of the partial pressure of NO, divided by the product of the partial pressure of N<sub>2</sub> multiplied by the partial pressure of O<sub>2</sub>, for any mixture of these three constituents in equilibrium at 2400° C. will be equal to 0.0032. Through the application of thermodynamic principles,<sup>1</sup> it is possible to calculate the value of *K'* for any other temperature from the above experimentally determined value of *K* for 2400° C. From this value of *K'* for any other temperature, as 3000° C., for example, it becomes a simple matter to calculate the yield of NO which will be obtained from any initial mixture of nitrogen and oxygen brought to equilibrium at that temperature. Percentages of N<sub>2</sub>, O<sub>2</sub>, and NO which satisfy the equilibrium relationship for any temperature will always be obtained when these constituents are brought to equilibrium at that temperature. Further, the reaction is reversible, and reaches the same results from either direction. A number of values for equilibrium constants of this reaction at different temperatures have been calculated. From these values the percentage yield of NO from air has been calculated, and the calculations have been checked, as follows:<sup>2</sup>

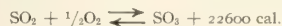
TABLE I—COMPARISON OF CALCULATED AND OBSERVED VALUES OF EQUILIBRIUM CONSTANTS FOR THE  $\text{N}_2 + \text{O}_2 \rightleftharpoons 2\text{NO}$  REACTION

Temperature °C.	NO (calculated from values of <i>K</i> Per cent	NO (observed) Per cent
1538.....	0.35	0.37
1604.....	0.43	0.42
1760.....	0.67	0.64
1922.....	0.98	0.97
2307.....	2.02	2.05
2402.....	2.35	2.23
3060.....	5.00	

It is observed that until 3000° C. is exceeded the yield of NO is below 5 per cent. The above clearly indicates how theoretical considerations show the limits of a reaction as well as the most favorable conditions for its industrial application. The oxidation-of-nitrogen process obviously is limited in practical application to localities where large quantities of cheap electric power are available.

#### CONTACT PROCESS OF MANUFACTURING SULFURIC ACID

The contact process of manufacturing sulfuric acid, considered from the equilibrium view point, can be expressed by the equations:



$$K = \frac{p_{\text{SO}_3}}{p_{\text{SO}_2} p_{\text{O}_2}^{1/2}}$$

A few values of *K* follow:<sup>3</sup>

TABLE II—CONSTANTS FOR CONTACT PROCESS OF MANUFACTURING SULFURIC ACID

Temperature °C	<i>Kp</i> (experimental)
400.....	580 (calculated)
450.....	188
515.....	65.4
600.....	14.9
800.....	1.81
900.....	0.57

Upon calculating the maximum yields of SO<sub>3</sub> obtainable at the different temperatures from the various values of *K*, it is

<sup>1</sup> Nernst, "Theoretical Chemistry," 7th German edition, pp. 525-6; Morgan, "Elements of Physical Chemistry," 5th edition in press.

<sup>2</sup> Nernst, *Z. anorg. Chem.*, **1906**, pp. 213-228; Z. f. Elektrochem., **1906**, pp. 257, 529; Jelinek, *Z. anorg. Chem.*, **1906**, pp. 229-276; Nernst-Finckh, *Z. anorg. Chem.*, **1905**, p. 116.

<sup>3</sup> Knietzsch, *Ber.*, **1901**, p. 4069; Bodländer, u. Köppen, *Z. f. Elektrochem.*, **1903**, p. 787; Bodenstein u. Pohl, *Ibid.*, **1905**, p. 373.

<sup>1</sup> Nernst-Finckh, *Z. anorg. Chem.*, **1905**, p. 116; *Ibid.*, **1906**, pp. 212, 229.

observed that the yield rapidly decreases as the temperature increases. This is in contrast to the nitric oxide illustration where the yield of NO from N<sub>2</sub> and O<sub>2</sub> increases with the temperature. As the temperature increases in the SO<sub>2</sub> + O<sub>2</sub> reaction the values of the equilibrium constants decrease rapidly. At temperatures below 400° C., however, the union of SO<sub>2</sub> and O<sub>2</sub> is too slow for an industrial process. At this temperature there is but a slight sacrifice of the percentage of SO<sub>2</sub> and O<sub>2</sub> combination.

Temperature, however, is not the only thing which influences a reaction of this nature. Without entering into a mathematical discussion of the influence of pressure we can recall LeChatelier's principle: that pressure stimulates those reactions involving contraction, while vacuum encourages those reactions involving expansion.

Further, temperature and pressure do not complete the factors influencing chemical reactions where equilibria are involved. The third and important factor is the relative concentration of the various reacting elements. The SO<sub>2</sub> reaction furnishes an excellent example showing the influence of the concentration of the combining reagents. Observing the mathematical expression for the equilibrium relationship,

$$K = \frac{p_{\text{SO}_2} p_{\text{O}_2}^{1/2}}{p_{\text{SO}_3}} \quad \text{or} \quad \frac{p_{\text{SO}_2}}{p_{\text{SO}_3}} = K \sqrt{p_{\text{O}_2}}$$

it becomes evident that the relative yield of SO<sub>3</sub>, with respect to SO<sub>2</sub>, increases as the partial pressure of oxygen increases, since the value of  $K$  for any given temperature does not change. This can best be observed by giving  $K$  the arbitrary value 200, and assigning to O<sub>2</sub> the partial pressures 0.25, 0.50, 1.00 and 2.00: Then

$$\frac{\text{SO}_2}{\text{SO}_3} = 200 \sqrt{\text{partial pressure O}_2}$$

and the ratios desired are given below:

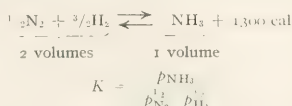
TABLE III—EFFECT OF CHANGING THE CONCENTRATION OF ONE OF THE CONSTITUENTS IN AN EQUILIBRIUM

Partial pressure of oxygen	Ratio of SO <sub>2</sub> to SO <sub>3</sub>
0.25	100
0.50	141
1.00	200
2.00	282

This influence of an excess of oxygen is of practical value and is used in the commercial manufacture of SO<sub>3</sub>.

#### SYNTHESIS OF AMMONIA FROM HYDROGEN AND NITROGEN

Another illustration of the factors entering into chemical equilibria involving temperature, pressure, and concentration is the Haber method of manufacturing ammonia from nitrogen and hydrogen.<sup>1</sup> The synthesis of ammonia from nitrogen and hydrogen depends upon the equilibrium represented by the expression,



A few investigated values for  $K$  follow:<sup>2</sup>

TABLE IV—EQUILIBRIUM CONSTANTS FOR THE AMMONIA SYNTHESIS

Temperature °C	K (experimental)	K (calculated)
700	0.00033	0.00036
800	0.00033	0.00036
1000	0.000148	0.000145

Haber<sup>3</sup> found that as the temperature rises above 500° C., the yield of NH<sub>3</sub> is low, while below 500° C., the rate of reaction is too slow. He eventually so perfected his experimental apparatus that his yields of NH<sub>3</sub> permitted him to calculate  $K$  from experimental data and compare the same with theoretical values.

<sup>1</sup> Zeitsch. f. Elek., 1913, p. 53.

<sup>2</sup> F. Haber, "Thermodynamics of Technical Gas Reactions."

<sup>3</sup> F. Haber, THIS JOURNAL, 6 (1914), 325.

The close correspondence of the theoretical and actual values indicates how experiment reinforced by theory will often show what can be expected in practice better than imperfect experimental results without theory. Without theory, in fact, Haber would never have known whether his experimental work was perfect, imperfect, or worthless.

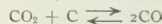
In this ammonia reaction, equilibrium relations are such that when the reaction is practiced under atmospheric pressure the maximum yield is not sufficient to warrant industrial application. A yield of less than one-quarter of one per cent is of little more than scientific interest. Through the introduction of increased pressures, however, the contraction from two volumes to one volume is greatly favored and the process yielding twelve per cent at once becomes of decided commercial interest. In the oxidation-of-nitrogen process, on the other hand, there is no change in the number of volumes, and pressure is without influence on the reaction. This pressure influence in connection with equilibrium relations is strikingly shown in Table IV.<sup>1</sup>

TABLE V—PERCENTAGE OF NH<sub>3</sub> IN THE EQUILIBRIUM OF THE REACTION N<sub>2</sub> + 3H<sub>2</sub>  $\rightleftharpoons$  2NH<sub>3</sub>

Pressure in atmospheres	Temperature °C.				
	550	650	750	850	950
100	0.0769	0.0321	0.0159	0.0089	0.0055
100	6.70	3.02	1.54	0.874	0.542
200	11.9	5.71	2.99	1.68	1.07

#### OTHER APPLICATIONS OF EQUILIBRIUM RELATIONS

The equilibrium relationship between reacting agents persists throughout all chemical phenomena. The relative amount of CO<sub>2</sub> to CO issuing from a furnace is primarily a function of temperature and pressure, and is influenced by the machine only in so far as the machine influences these variables. The equilibrium between CO<sub>2</sub> and CO in the presence of carbon for any temperature is reached regardless of whether one starts with CO or with CO<sub>2</sub>, or with any mixture of the two.

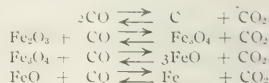


$$K = \frac{p_{\text{CO}}^2}{p_{\text{CO}_2}}$$

TABLE VI—EQUILIBRIUM RELATIONS BETWEEN CO AND CO<sub>2</sub> IN PRESENCE OF CARBON

Temperature °C.	Per cent by volume	
	CO	CO <sub>2</sub>
450	2	98
750	76	24
1050	99.6	0.4

Typical examples of this relationship are found in the kitchen stove, the factory boiler, the blast furnace, the gas machine or the open hearth furnace. Doubling the size of the blast furnace changes the relative amounts of CO<sub>2</sub> and CO only so far as doubling the size of the furnace influences the temperature in the various reacting zones. With increasing temperature the percentage of CO increases, with decreasing temperature the percentage of CO<sub>2</sub> increases. In the blast furnace, for instance, not only are the CO and CO<sub>2</sub> in equilibrium, but the various oxides of iron are likewise in equilibrium with carbon, CO and CO<sub>2</sub>, as well as with one another. Consider the blast furnace reactions:



from the equilibrium point of view; there is found to be a vital relationship between them. On first sight a series of equations of such a nature looks very complex, but on the application of equilibrium relationships, formulated by means of the phase rule diagram, it is found to be relatively simple and clear. Experimental work<sup>2</sup> has been done on these relationships, from which it is possible to plot the diagram of equilibria.

<sup>1</sup> J. Mellor, "Modern Inorganic Chemistry," p. 713.

<sup>2</sup> Baur and Glaessner, Z. physik. Chem., 1903, p. 354.

All of the reactions are reversible, their direction is entirely a function of temperature. From the diagram, the fields of stability of Fe, FeO and  $\text{Fe}_3\text{O}_4$  in the presence of CO and  $\text{CO}_2$  for the temperatures shown can be observed. It can be noted for example, that FeO at  $650^\circ\text{C}$ . is not stable in the presence of more than 65 per cent or less than 43 per cent  $\text{CO}_2$ . It becomes evident that in the reduction of FeO to Fe a maximum of

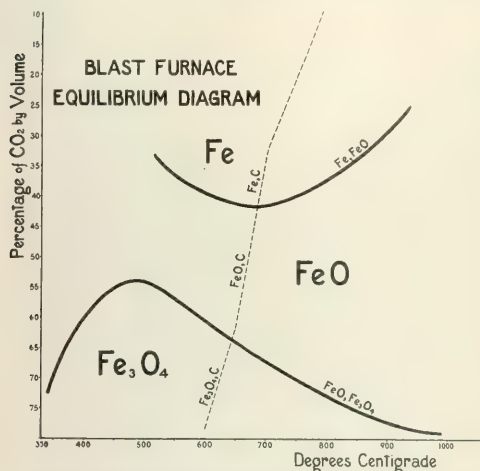


FIG. 1 BLAST FURNACE EQUILIBRIUM DIAGRAM, SHOWING RELATIONS BETWEEN C,  $\text{CO}$ ,  $\text{CO}_2$ , Fe, FeO, and  $\text{Fe}_3\text{O}_4$

$\text{CO}_2$  in the flue gases is obtained when the reaction takes place at about  $675^\circ\text{C}$ ., and that this percentage of  $\text{CO}_2$  decreases as the temperature increases. The diagram indicates that most of the reduction takes place in the cooler part of the furnace.

#### COEFFICIENT OF PARTITION OR DISTRIBUTION

Equilibrium conditions also prevail in the more purely physical world as well as in chemistry. A solute which divides itself between two immiscible solvents will always be found in a definite concentration in both solvents, and there will always be a definite ratio between the concentration in each. This ratio is known as the partition or distribution coefficient. I will cite first the laboratory example dealing with iodine, water and carbon disulfide. Iodine is slightly soluble in water and much more soluble in carbon disulfide, while water and carbon disulfide are practically insoluble in each other. Suppose we have both water and carbon disulfide in one vessel and add some iodine. It has been observed from experiments that the concentration of iodine in the carbon disulfide is 588 times the concentration of iodine in water. In other words,

$$K_{\text{Iodine}} = \frac{C_{\text{CS}_2}}{C_{\text{H}_2\text{O}}} = 588$$

In similar manner, iodine divides itself between ether and water so that the concentration of iodine in the ether is 200 times the concentration of iodine in the water.

$$K_{\text{Iodine}} = \frac{C_{\text{ether}}}{C_{\text{water}}} = 200$$

Similar examples can be found in the distribution of acetic acid between benzene and water, benzoic acid in benzene and water, succinic acid in ether and water, acetic acid in chloroform and water, saccharin in ether and water, acetanilid in ether and water, vanillin in ether and water, or acetanilid in chloroform and water. This aspect of equilibrium is finding application in analytical chemistry, more especially in that branch dealing with alkaloids.<sup>1</sup>

Through its application the haphazard washing out process in alkaloid work is replaced by one of mathematical precision. Technical application can be found in Parke's process for extracting silver from lead. Silver is very much more soluble in zinc than in lead, whereas lead and zinc are only slightly soluble in each other. The lead containing silver is melted and thoroughly mixed with a small proportion of zinc. The zinc floats to the top, carrying with it in solution practically all of the silver, and on cooling solidifies while the lead is still molten. The zinc containing the silver is then skimmed off, and these two constituents separated.

Lack of time forbids the consideration of the equilibrium relationships existing in the ionization of acids, bases and salts. Their application in analytical chemical methods is today a reality; their technical application promises much.

#### EQUILIBRIUM RELATIONS ARE OF GENERAL APPLICATION

The equilibrium or kinetic relationship is accepted and used by theoretical chemists, and is believed to prevail in practically all fields of chemistry. When considered in mathematical units it changes qualitative suggestion into quantitative information. Equilibria deal with yields in terms of percentages or weights, they deal with temperature, pressure and concentration in numerical terms. When so applied, they are concrete and cease to be more theoretical than any other mathematical statement.

Equilibria exist between reacting agents in solution; between reacting liquids; between liquids and vapors; solids and liquids; solids and gases; between gases which react chemically; between the concentrations of a solute divided between two immiscible solvents; in the ionization of acids, bases and salts, in hydrolysis and saponification; in fact in all the chemical and physical phenomena with which the chemist or the chemical engineer deals. The industrial development and application of physical chemistry, including this equilibrium principle, is only partially realized today; its further development and application seem to depend largely upon competition and necessity, and the stimulus they offer to the inventive faculties of chemical engineers as the leading specialists in this most promising field of our science.

CHEMICAL ENGINEERING LABORATORY  
COLUMBIA UNIVERSITY  
NEW YORK

#### STANDARDS OF FOOD AND DRUG CHEMISTS<sup>1</sup>

By EDWARD GUDEMAN

The Food and Drug chemists are those who today are and should be vitally interested and concerned with the health and well-being of the inhabitants of communities, state and nation. What is the standing of the chemists in the United States, not as we see ourselves but as others see us? In fact do we as a profession exist at all? Have we any rights or standing and if so, where, what are they, how do we get them and what do they amount to, outside of our own family circle?

I broached this matter before our local Chicago Section and was told that my remarks were funny, which recalled to me what a great German poet and philosopher said—"Die Sache wäre lächerlich, wäre sie nicht so fürchterlich," freely translated as—"The matter would be laughable, were it not so terrible."

Have you recognized that every great discovery or advancement, made within the last decade or two, that directly affects the health and well-being of the human race, depends directly on chemistry and its application? All advances and progress in biology, physiology, medicine, pharmacy, dentistry, veterinary practice, sanitation and health protection of the individual or community is directly based on a chemical foundation. Let me illustrate with a recent publication, *Science*, March 27, 1914, "Action on Vital Stains, Etc," by Evans and Schulemann,

<sup>1</sup> Presented at the 49th Meeting of the American Chemical Society, Cincinnati, April 6-10, 1914.

<sup>1</sup> J. W. Marden, *THIS JOURNAL*, 6 (1914), 315.



giving the results of biological, physiological, medical research work affecting the human body, based directly on the most modern branch of chemistry, that of the colloids. Not alone internal medicine, but surgery of today uses chemical substances to act on the nerves or nerve centers to overcome "shock." Are we not today, in the chemical laboratories, separating and manufacturing the substances that cause toxic and anti-toxic effects? Do we not know today that digestion is not due to "organs" or a "vital" force, but that it is a direct analytical or synthetic chemical process? Do we not produce today outside of the animal body the exact products that are produced in the body? I am certain that many diseases will, within a reasonable time, be greatly benefited by direct chemical treatment. As a special example I wish to cite the use of sulfurous acid fumes and chemical anti-toxic serums in the treatment of the early stages of tuberculosis.

We use many descriptive adjectives in connection with our profession, such as medical, biological, physical, electrical, pharmaceutical, sanitary and XYZ chemistry, making our profession the handmaid to the other professions. Let us see where the agricultural, food or drug chemist stands today compared with other professions, such as the medical, pharmaceutical, veterinary and legal professions. Is it not true that to practice any of these professions in most states or communities, a diploma from a recognized institute of learning is required, besides a special license or permission to practice? Is not such license issued only by some board or commission or committee, on whom is conferred, often by legislative act, the right to issue such permit? The granting of such license, with or without special examination, carries with it the legal right to kill or cure, the right of depriving you of your liberty for a greater or lesser time. All these professions have conferred on them the legal or public right to render their verdict of "to be or not to be." Where does the chemist come in? We do not even get the leavings. "There ain't no core" for us, as the other professions are individually or collectively the whole thing, and we chemists are the bung-hole of the barrel, a perfect nothing.

It is true that a limited number of chemists have some "recognized" standing. I refer to the so-called "official" chemists. Who are they as a body, and what makes them "official," and what does the designation "official" mean? Anybody or any concern, any school, college or university, private or incorporated, can attach to itself a chemist and immediately such chemist becomes the "official" chemist of the party, concern or institution, and remains such official chemist as long as he remains on the payroll, with the loss of the position goes the "official" standing. I am not against the "official" chemist as I have to admit that I am one myself.

Now what standing has an "official" chemist? Many of you may agree or disagree with me, that as soon as one qualifies in court as an "official" chemist, more weight is given to the testimony, than to that of the non-official chemist, without due consideration to the ability or capability of the chemists involved. Often the qualification as an "EX Official" gives extra weight to the testimony. Often official chemists from the same laboratory testify on collaboration work, thereby getting the double advantage of that due to the "official" standing and the preponderance of testimony. It is unfortunate that the courts often hold the testimony of the "official" chemist as being neutral and unprejudiced, and the testimony of the non-official chemist as that of a partisan. This applies more especially to official chemists connected with city, state or national bodies. My own observation has been that there are as many non-partisan non-official chemists as there are partisan official chemists, and I have also found that change from "official" to "non-official" chemist often carries with it a quick and radical reversal of opinion.

The chemical profession is not recognized as it should be,

since we have no legal or legislative standing, such as have the other professions mentioned. It is a fact that in the State of Illinois, you cannot run an automobile or an engine, nor a barber-shop, nor can you be a boot-black, nor an undertaker, without having a special city or state license to practice these professions, and in many cases a special examination is required to obtain the license. I am perfectly aware that many "official" chemists qualify through having passed civil service examinations. Those of us who have passed this ordeal and gone through this farce, will also agree that the less said about these examinations the better for the chemical profession.

Bills introduced into our legislative bodies, city, state or nation, are good barometers indicating the standing of our profession in the eyes of our law makers. I shall take up only one such bill, a Federal bill, as it is fully up to the average. This bill defines the term "DRUG" as any substance to be used for the cure, mitigation or prevention of disease of man or other animals, and includes among the drugs also soda and potash lye, cosmetics, tobacco, snuff, tobacco substitutes and all other tobacco products. The bill then shows up the chemists by requiring " \* \* \* \* \* or any other drug or medicinal preparation which is not marked to show that it has been MANUFACTURED or COMPOUNDED by a legally registered or qualified practitioner of MEDICINE or PHARMACY who holds an unsuspended or unrevoked license issued by the Secretary of Agriculture both in the state in which said PHYSICIAN or PHARMACIST resides and in the state in which the said remedy IS TO BE SOLD \* \* \* \* \*"

Also: "All these articles or preparations when offered for sale, except prescriptions of LICENSED practitioners of MEDICINE or DENTAL-SURGERY or VETERINARY SURGEONS in the course of their personal practice shall bear a label containing not only the name by which they are known but also the names of the parent substances from which they are derived."

This bill creates a monopoly for the medical man and the pharmacists in the manufacture of food and drug products. There are some very good points in the bill, as tobacco, snuff and other tobacco products must come up to a fixed standard. You must be sure that you do not handle any smoking, chewing or snuffing tobacco that: "consists in whole or in part of filthy, decomposed or putrid animal or vegetable matter." It may be on account of the animal matter in tobacco that the bill recognizes the veterinary profession. The exclusion of some kinds of vegetable matter from tobacco may help reduce the high cost of living, by forcing back into its natural food channel—cabbage. Another excellent point in this bill is that it does away with the misunderstanding as to "like substances" found in the Food and Drugs Act of June 1906. This new bill does not recognize that term and replaced it with the easily understood term of "similar substances."

As I do not want to start any discussion on State Rights, I have selected a bill introduced into Congress by a member from Illinois.

Does it not strike you as peculiar, to use a very mild expression, to find legislative acts, enumerating a large number of drugs and chemical products, or derivatives of parent chemical products, pure chemicals and synthetic products of the chemical laboratories, all full-fledged children of chemistry, not even half-orphans, and the chemists, the natural parents or guardians of their offsprings, ABSOLUTELY IGNORED, and the manufacture and sale directly placed under the supervision of only distant relatives, those belonging to the MEDICAL, PHARMACEUTICAL or VETERINARY professions? What is the reason? Is it due or partly due to the fact that anybody can call himself a chemist in the UNITED STATES and get away with it? Is it because the standard or quality of any food or drug can be passed on by anybody? Is it not time for the chemists, especially those who are interested in the health and welfare of their fellow beings,

to do something, to get the recognition due them and to place the profession on the high plane which it should occupy? In Illinois the only two SCIENTIFIC professions that can be followed by anyone without license, or permit, or qualification to practice, are those of COOKS and CHEMISTS. What shall we do and what is the cure, remedy or prevention? Is it not time for the CHEMIST to take a stand for a standard of the CHEMIST?

POSTAL TELEGRAPH BUILDING, CHICAGO

### THE CHEMIST, A GROWING FACTOR IN MERCHANDIZING<sup>1</sup>

By A. V. H. MORGAN

That the chemist has for some time been a very important factor in manufacture is everywhere well recognized. On the other hand, his employment by the consumer has been practically limited to the extent that the manufacturer is also a consumer. Until recently the small consumer has enjoyed the benefits of chemical control only to the extent that control of raw materials and improvement of processes of manufacture work indirectly to his advantage.

Under the old trade maxim, "Let the buyer beware," the need for more than off-hand inspection of purchases on the part of the small consumer has been great, but his ability to afford such inspection plainly negligible.

At an early day little protection was needed by the consumer since many of the necessities of life, and such luxuries as were afforded, were produced at home. Later, when the factory began to replace the kitchen, the churn, the spinning wheel and the loom, and powdering, mixing, coating, coloring, flavoring and preserving frequently made the original raw material well-nigh unrecognizable, sophistication became increasingly difficult of detection. With the introduction of package goods and the necessary label came also the opportunity and temptation to misrepresent.

It is well to remember in this connection, however, that the beginnings of adulteration and misbranding were certainly the work of only a relatively small class in the community—the unfair minority—though it must be admitted that with unfair competition thus set up, the relatively honest majority too often felt the necessity of meeting such competition in kind.

The introduction of these abuses was naturally a gradual process, as was also the development of resentment on the part of the consumer, but the latter finally began to feel that under our form of government, in which the majority is at least entitled to rule, the interest of the consumer, who is in the vast majority, is certainly the matter of first consideration. This awakening public sentiment has caused the enactment of commodity laws, which though designed originally to protect the consumer, are bound to result through the elimination of unfair competition in great good to the majority of producers and distributors as well.

This "business honesty" legislation began with laws governing the character and description of commodities related in part to the matter of public health, *viz.*, foods and drugs, but has already been supplemented by laws regulating the character and description of other commodities and is rapidly spreading in its application to the whole business fabric. The public sentiment that is bringing this about is no doubt being influenced by the fact that the enforcement of these food and drug laws has uncovered more of simple fraud than of injury to health. As greatly to be desired, therefore, as is the protection of the health of the people, still, where health is not involved, there is no logic in requiring a higher standard of honesty for one class of commodities than for another. As there can be no doubt of the permanency of these initial laws, we may expect the future to give us laws designed to eliminate fraud not only from foods and

drugs but from commodities in general. A beginning made in the case of insecticides, paints, and honest weights and measures, is destined soon to be extended to include textiles, metals and other commodities whose off-hand valuation is difficult or impossible.

Again since the individual consumer has little or no opportunity to protect himself when off-hand inspection is inadequate, we are coming to recognize that, as representing the vast majority of the people, he is entitled to the protection that comes from placing the responsibility as to quality and description upon the producer and distributor. And so it is that the old rule of trade, "Let the buyer beware," is giving place to the more logical and fair requirement, "Let the seller beware," a principle which finds its natural expression in the commodity law.

Though this new rule of trade is coming in through the demand of the buyer, still the far-sighted seller is beginning to look upon it as more of an asset than a liability. He knows that permanent success must rest on the continued satisfaction of the buyer, and that this satisfaction may be depended on to continue only so long as he, the seller, is willing to take upon himself the obligation of seeing that the quality, as well as the price, is right. Furthermore, he knows that the degree of the buyer's satisfaction depends not entirely on value, since the buyer may not be a good judge of values, but depends rather on the ratio between realization and expectation—a fact suggesting the disadvantage of extravagant advertising. Accordingly, the merchant is coming to believe that the only permanent basis of successful merchandizing, at least in this day and age, lies in the sale of none but dependable goods, and that through a medium of advertising that is both truthful and accurate.

The notion that the merchant's obligation is fulfilled when he sells his wares simply for what they are represented to him to be is rapidly passing, along with the fallacy that the press has no responsibility for the character of its advertising matter. Likewise the merchant who hides behind the excuse that he has no way of knowing whether or not his goods are what they are represented to him to be, is going to have to give way to the merchant who acquires means of finding out.

It is here that the chemist makes his entrance. His is the work of appraising value when off-hand inspection proves inadequate—the work of finding the small percentage of cotton in the "all wool" suit, an adulterant which the touch of the expert might fail to reveal; of finding the same cheaper fiber that may lessen the value of the linen table cloth and the silk dress; of determining whether or not the filled gold watch is indeed worthy of the name; whether the linseed oil is true to name and the turpentine not obtained in part from mother earth or from another cheap source. Indeed the merchandise chemist's problems may well be many, if he turn his attention to all that might be improved through his criticism. If his work lie in the field of foods, drugs, insecticides, or in any other covered by inspection laws, he has the added responsibility of protecting his employer from the bad advertising that even being the distributor of illegal goods is likely to entail. The guaranty of the seller may be depended on to forestall prosecution, but ignorance as an explanation of the possession of contraband goods cannot be expected to satisfy the customer. There is therefore a growing suspicion that the safe course lies in criticizing one's own product more severely than any public official would have the heart to.

Possibly some may be thinking of our merchandise chemist as an analyst, pure and simple, but he must be more than this. To be sure, analysis must precede criticism, but criticism, which is the interpretation of analysis—the rendering of an opinion as to value—is the service really required.

As value is a purely relative matter, no opinion worth while is possible without a standard for comparison. The selection of

<sup>1</sup> Presented at the 49th Meeting of the American Chemical Society, Cincinnati, April 6-10, 1914.

suitable standards is a work of first importance, therefore, and one of no little difficulty. Much along this line has been and is being done by various organizations, but a much greater part remains to be done. With the advent of commodity laws has naturally come greater attention to standards as a necessary basis of criticism of both product and label, and much of value is to be expected from this source.

We turn aside to observe, in this connection, that these commodity laws can scarcely serve the consuming public better than through the establishment of standards specifying properties and constituents, and even origin and method of production when necessary, since the general adoption of such standards will tend in the long run not only to improve quality but to reduce the cost to the consumer. We hear much of the advantage by way of uniformity of quality, that is associated with proprietorship and the "coined name," but this advantage too often costs the public much more than it is worth. The justice of rewarding the author of a new and useful idea, as voiced in our patent laws, is easily granted, but the collection of tribute through the employment of secrecy and much advertising is quite another matter. When superiority is measured largely or entirely in terms of printer's ink, the consumer pays the printer and gets little or nothing but misinformation for his added expenditure. The remedy for such abuses must come, in part at least, through the adoption of commodity standards.

In this work of the preparation of standards, in fact, wherever opportunity offers, the merchandise chemist may logically join

hands with those engaged in the enforcement of commodity laws, since such laws are now generally acknowledged to give expression to the principles underlying permanent success in his own field. He must furthermore keep in close touch with all the laws that affect his goods, for he must conform to the letter as well as to the spirit of the law.

It is plainly this necessity of meeting the requirements of commodity laws, present and to come, that is largely responsible for the growing demand for the chemist in the field of merchandizing. It is important to note in this connection that though our present commodity laws have come through the demand of the consumer, our future laws of this sort are likely to be welcomed (as is the continuance of our present laws desired) by the business world, which is coming to look upon success as something to be attained through service rather than through exploitation, and is tending to be guided by an enlightened self-interest that welcomes the law that commands strict obedience to basic principles of honesty, since thereby comes the elimination of unfair competition.

That we are destined to have general commodity laws in the not distant future appears certain. Even without the necessity of law obedience a broad merchandizing policy is already finding much need for the chemist. With the coming of general commodity laws there will be added many new fields in which the importance of the chemist's work will amount to a necessity.

CHICAGO

## CURRENT INDUSTRIAL NEWS

By M. L. HAMLIN

### CHEMICAL INDUSTRY AND TRADE IN AMERICA IN 1913

In an article in *Chemie*, June 6, 1914, a large amount of statistical data concerning chemical trade in this country appear. It is as yet too early to gain from these data any precise information as to the permanent effect of the new tariff on this branch of foreign trade, but it is stated that the imports of chemicals, drugs, dyes and medicines in November and December of last year were about five million dollars less than in the same months of the previous year, while the value of these articles imported during the whole of 1913 was in round numbers \$101,000,000 as compared with \$87,000,000 in 1912. Of these materials, goods to the value of \$67,000,000 came in duty-free. The exports of these classes of articles amounted to \$27,000,000 in 1913 and \$26,000,000 in 1912.

In general, chemical technology is not as advanced in this country as in Europe, and it is those things that are manufactured by comparatively simple methods, such as sulfuric acid, soap, cement, petroleum products, and vegetable oils that form the bulk of American chemical manufactures. While the manufacture of complicated organic products like artificial perfumes has increased greatly in the last few years, the inorganic and electro-chemical fields are the most highly developed.

The petroleum trade in its relation to Germany is shown in the following table:

	OIL EXPORTS TO GERMANY		
	1911	1912	1913
Light oils	\$5,510,000	\$5,502,000	\$4,526,000
Lubricating and heavy paraffin oils	2,628,000	3,284,000	3,661,000

Exports of gasoline have increased enormously but the amount sent to Germany is not given in the statistics. In 1913, Belgium imported \$276,000 and Holland \$905,000 worth, while to the rest of Europe the United States sent \$4,600,000 worth.

The chemical and related imports into and exports from the United States in 1913 were as follows:

	IMPORTS	
	1912	1913
<b>CHEMICALS</b>		
Arsenic and arsenic sulfide	\$ 247,000	\$ 276,000
Calcium chloride	597,000	510,000
Calcium nitrate	689,000	500,000
Iodine	737,000	521,000
Magnesia	1,266,000	1,669,000
<b>Acids</b>		
Carbolic	706,000	558,000
Acetic	51,000	
Oxalic	372,000	368,000
Other acids, duty free	408,000	383,000
Other acids, dutiable	217,000	533,000
<b>POTASSIUM SALTS</b>		
Potassium carbonate	\$658,000	\$653,000
Caustic potash	366,000	246,000
Caustic potash, not less than 15 per cent caustic soda		89,000
Potassium cyanide	170,000	105,000
Potassium chloride	7,229,000	7,120,000
Potassium sulfate	1,770,000	1,633,000
Saltpeter, crude	216,000	263,000
Other salts	317,000	555,000
<b>SODIUM SALTS</b>		
Sodium nitrate	\$16,554,000	\$21,631,000
Other salts	302,000	325,000
<b>AMMONIUM SALTS</b>		
Ammonium chloride	\$ 553,000	\$ 466,000
Ammonium sulfate	3,447,000	3,957,000
Sulfur	495,000	278,000
Iron pyrites	3,861,000	3,611,000
Tartar, crude	2,526,000	2,779,000
<b>MEDICINES, DRUGS, ETC.</b>		
Opium (at least 9 per cent morphine)	\$2,220,000	\$2,391,000
Opium from England	489,000	269,000
Opium from Turkey	1,614,000	1,910,000
China bark	310,000	367,000
Quinine, all forms	482,000	562,000
Medicinal preparations	1,642,000	1,430,000
Amyl alcohol	1,336,000	1,087,000
Hops	2,592,000	2,946,000
Licorice	1,806,000	1,775,000
Vanilla beans	2,528,000	2,530,000
Mineral water	967,000	993,000
<b>FERTILIZERS</b>		
Guano	\$ 336,000	\$ 538,000
Bone meal	847,000	837,000
Kainite	2,386,000	2,207,000
Salts	1,795,000	2,150,000
Other fertilizers	3,528,000	4,996,000



OILS, WAXES, ETC.		1912	1913	PAINTS, VARNISHES, ETC.		1912	1913
<b>Ethereal oils:</b>				<b>Zinc oxide</b>		1,248,000	1,136,000
Lemon oil		\$ 511,000	\$ 721,000	White lead		481,000	905,000
Other ethereal oils, duty-free		2,542,000	2,804,000	Lamp-black		659,000	470,000
Other ethereal oils, dutiable		1,064,000	1,196,000	Ready mixed paints		589,000	1,167,000
<b>Tree oils:</b>				Lacquers and varnishes		1,230,000	1,107,000
Cocoa butter		1,238,000	1,223,000	Other related articles		2,822,000	1,819,000
Cocoonut oil, crude		3,865,000	6,258,000	Printer's inks		214,000	435,000
Linseed oil		193,000	87,000	Other like oils		214,000	197,000
Cottonseed oil		117,000	734,000	Blacking		75,000	698,000
Peanut oil		670,000	1,038,000	Pencils		292,000	611,000
Chinese nut oil		2,829,000	2,370,000	<b>NAVAL STORES</b>			
Olive oil, technical		469,000	369,000	Turpentine		9,372,000	8,158,000
Olive oil, table oil		7,147,000	6,777,000	Rosin		16,376,000	13,563,000
Waxes		698,000	712,000	Tar, pitch, etc.		217,000	529,000
Palm oil		3,443,000	3,631,000	<b>OILS</b>			
Palm oil, from seed		2,139,000	2,445,000	<b>Vegetable oils:</b>			
Soya bean oil		1,361,000	693,000	Cottonseed oil		21,928,000	17,991,000
Fish and cod liver		882,000	834,000	Exported to Germany		1,150,000	889,000
Mineral oils, crude		4,656,000	10,945,000	Linseed oil		1,438,000	1,219,000
Benzene, gasoline, naphtha		1,218,000	1,472,000	Other like oils		279,000	784,000
Other oils		159,000	580,000	Animal oils, total		353,000	418,000
Wax, mineral		489,000	555,000	Fish oil (not cod liver oil)		1,339,000	1,250,000
Wax, vegetable		1,088,000	1,146,000	Mineral oils and crude oil		6,770,000	319,000
Glycerine, crude		3,655,000	4,695,000	Other like oils		62,084,000	72,042,000
Olive oil residue		925,000	717,000	Illuminating oil		28,297,000	29,609,000
Other fats and oils		706,000	439,000	Lubricating and paraffine oils		54,672,000	\$17,419,000
Gelatin		129,000	624,000	Naphtha and other light distillates		15,788,000	10,674,000
<b>DYES AND TANNING MATERIALS</b>				Gasoline		4,111,000	9,990,000
Alizarine and alizarine dyes		\$1,504,000	\$1,493,000	Other light oils		2,488,000	1,134,000
Coal tar dyes		7,317,000	7,111,000	Gas and fuel oil		9,603,000	8,177,000
From Germany		6,001,000	5,778,000	Paraffine			
From England		232,000	239,000	<b>SOAPS AND TOILET ARTICLES</b>			
From Switzerland		835,000	839,000	Toilet soaps		2,006,000	2,185,000
From other countries		258,000	256,000	Other soaps		2,635,000	2,672,000
Aniline salts		354,000	334,000	Perfumes, etc.		1,280,000	1,575,000
Indigo, natural and synthetic		1,212,000	1,469,000	Raw materials for soap manufacture		4,619,000	5,117,000
Paints, pigments, varnishes		512,000	469,000	<b>EXPLOSIVES</b>			
Logwood		512,000	469,000	Cartridges		2,507,000	3,015,000
Dye woods		44,000	86,000	Dynamite		1,301,000	1,498,000
Madder bark		395,000	245,000	Gunpowder		352,000	1,600,000
Quebracho wood		1,039,000	990,000	Other explosives		904,000	652,000
Sumach		380,000	218,000	<b>MISCELLANEOUS EXPORTS</b>			
Dye and tanning extracts		1,789,000	2,221,000	Mercury		13,000	44,000
Other tanning materials		339,000	401,000	Celluloid		1,880,000	1,317,000
Pencils and pencil leads		535,000	599,000	Waste rubber		869,000	768,000
<b>GUMS AND RESINS</b>				Graphite		343,000	392,000
Camphor, crude and natural		\$ 747,000	\$1,118,000	Cellulose		543,000	738,000
Camphor, refined and artificial		84,000	211,000	Glue		289,000	260,000
Chicle		3,276,000	5,120,000	Candles		257,000	253,000
Copal, Kauri and Dammer		2,081,000	3,193,000	Colophony		3,003,000	3,310,000
Gambir		876,000	658,000	Cement		6,160,000	4,271,000
Shellac		2,472,000	3,058,000	<b>CANADA'S FOREIGN TRADE IN CHEMICAL AND RELATED PRODUCTS</b>			
Other resins, duty-free		2,204,000	1,615,000	<b>Not strictly comparable with the figures of the previous article, but similar enough for a restricted comparison are the data of Canada's chemical exports and imports during the "Rechnungsjahr," 1912-1913, which appeared in an article in <i>Chemiker Zeitung</i>, 38 (1914), 643. During this period the total imports into Canada rose 23 per cent from \$547,500,000 in the previous year to \$675,500,000; of this amount Germany sent \$14,200,000 worth, an increase of \$11,100,000.</b>			
Other resins, dutiable		188,000	269,000	<b>The value of imports classified as drugs, dyes, chemicals and medicines in the year 1912-1913 amounted to \$17,029,000 as compared with \$12,360,000 in the previous year; \$788,000 worth of this came from Germany as compared with the previous years' \$512,000, an increase of 54 per cent. The imports in this class from the United States amounted to \$8,997,000.</b>			
<b>RUBBER AND RUBBER SUBSTITUTES</b>				<b>In the above mentioned class of imports the most important are the following:</b>			
Balata		\$ 668,000	\$ 792,000	<b>IMPORTS</b>		1911-1912	1912-1913
Guthule		5,625,000	2,130,000	Potassium salts (total)		\$ 333,000	\$ 428,000
Guttajutong		2,215,000	1,766,000	Caustic potash		30,000	30,000
Gutta-percha		1,577,000	209,000	Potassium chlorate		42,000	57,000
Caoutchouc		99,567,000	76,821,000	Potassium chloride and sulfate (crude)		117,000	195,000
Caoutchouc, waste		2,973,000	3,193,000	Potassium bichromate		274,000	26,000
Caoutchouc substitutes		92,000	97,000	Potassium ferro- and ferricyanides		13,000	21,000
Origin of caoutchouc imports:				Saltwater		109,000	88,000
Belgium		6,091,000	4,983,000	Sodium salts (total)		1,917,000	2,834,000
Germany		7,073,000	4,270,000	Caustic soda		911,000	303,000
England		35,358,000	31,754,000	Sodium carbonate		390,000	458,000
France		3,157,000	1,750,000	Sodium bicarbonate		52,000	62,000
Portugal		1,102,000	239,000	Sodium chlorate		55,000	20,000
Brazil		32,133,000	19,867,000	Sodium sulfate (crude)		274,000	108,000
East Indies		9,040,000	11,004,000	Sodium silicate (solid and dissolved)		63,000	77,000
Mexico		1,734,000	921,000	Chili saltwater		857,000	1,642,000
<b>MISCELLANEOUS IMPORTS</b>				Acids (total)		292,000	441,000
Asbestos		\$1,456,000	\$1,929,000	Tartaric acid (crystalline)		60,000	75,000
Asbestos goods		364,000	390,000	Alum.		122,000	176,000
Graphite		1,709,000	2,110,000	Ammonium sulfate		11,000	16,000
Platinum, crude		1,717,000	1,979,000	Ammonium nitrate		40,000	102,000
Platinum, in blocks, sheets, etc.		2,618,000	2,969,000				
Platinum, laboratory apparatus		160,000	105,000				
Coal tar preparations not otherwise listed, duty-free		1,004,000	1,035,000				
Coal tar preparations, dutiable		661,000	782,000				
Cresote oil		2,908,000	4,081,000				
Glue		1,733,000	1,852,000				
Perfumes and toilet articles		1,810,000	2,044,000				
Soap, Marseilles		408,000	348,000				
Other soaps		1,147,000	402,000				
Photographic paper		1,147,000	1,275,000				
Photographic plates and films		621,000	1,056,000				
Explosives		614,000	723,000				
Matchsticks		649,000	758,000				
Artificial silk		1,826,000	2,835,000				
Cement		94,000	134,000				
<b>EXPORTS</b>							
<b>CHEMICALS, DRUGS, ETC.</b>							
Calcium carbide		\$ 960,000	\$ 946,000				
Calcium acetate		1,891,000	2,158,000				
Sulfuric acid		94,000	498,000				
Other acids		372,000	381,000				
Copper sulfate		325,000	212,000				
Sulfur		1,076,000	1,600,000				
Methyl alcohol		413,000	857,000				
Dyes		414,000	508,000				
Tan bark extract		784,000	866,000				
Baking powder		44,000	506,000				
Washing powder		247,000	635,000				
Vaseline, etc.		1,606,000	1,480,000				
Ginseng		447,000	476,000				
Roots, herbs, barks, etc.		7,608,000	6,966,000				
Patent medicines							

IMPORTS	1911-1912	1912-1913
Salammoniac	\$ 39,000	\$ 56,000
Boric	122,000	113,000
Chloride of lime	122,000	107,000
Tartar (crystalline)	275,000	276,000
Cyanides	96,000	155,000
Mercury	61,000	78,000
Sulfur (crude)	466,000	760,000
Copper sulfate	88,000	132,000
Drugs (crude)	130,000	126,000
Celan	133,000	145,000
Glycerine (for explosives)	943,000	906,000
Glycerine (raw)	129,000	159,000
Glycerine (not classified)	46,000	25,000
Gums and resins	434,000	534,000
Chicle gum	2,005,000	3,052,000
Gambur	110,000	136,000
Medicines and chemical preparations (dry)	923,000	1,105,000
Medicines and chemical preparations (non-alcoholic)	61,000	103,000
Medicines and chemical preparations (all others)	132,000	145,000
Limaments, etc.	155,000	198,000
Disinfectants (non-alcoholic)	59,000	74,000
Bacteriological preparations	96,000	128,000
Aniline and coal tar dyes (total)	467,000	555,000
From Germany	187,000	228,000
From the United States		209,000
From Great Britain		77,000
From Switzerland		28,000
Indigo (paste and extract)	18,000	16,000
Extracts of logwood, quebracho, etc.	683,000	977,000
Dyes and tanning materials (crude)	162,000	171,000

The following imports were not included in the above classification but are of a similar character:

	1911-1912	1912-1913
Fertilizers (total)	\$ 620,000	\$ 663,000
Artificial fertilizers	445,000	540,000
Bone meal, ash, etc.	103,000	123,000
Kainite and other German potash (salts)	7,000	300
Phosphates	1,767,000	1,997,000
Paints and pigments (total)	1,767,000	1,997,000
Lead paints	219,000	260,000
Zinc white	341,000	465,000
Lampblack	80,000	93,000
Paris green	101,000	131,000
Pigments (not classified)	248,000	308,000
Metal pigments cobalt, copper and zinc oxide	118,000	138,000
Liquid fillers, protective paints, etc.	407,000	497,000
Inks (including printer's ink)	148,000	160,000
Varnishes, lacquers, etc.	163,000	190,000
Turpentine	629,000	576,000
Waxes	262,000	263,000
Soap (total)	1,121,000	1,333,000
Laundry soap	339,000	386,000
Castile soap	191,000	176,000
Pearline and other soap powders	109,000	138,000
Sapolo and sand soaps	128,000	197,000
Toilet soaps	351,000	416,000
Perfumes and toilet articles	547,000	667,000
Ethereal oils	261,000	350,000
Celluloid, xylonite, etc.	225,000	246,000
Gutta-percha, caoutchouc and manufactured articles of rubber	8,103,000	11,153,000
Coke	1,637,000	2,023,000
Glue, paste, etc.	284,000	363,000
Explosives	1,681,000	1,236,000
Cement	945,000	1,953,000
Sugar, molasses, etc.	18,152,000	19,226,000

The total exports from Canada amounted to \$393,200,000 in the year 1912-1913 and \$315,300,000 in 1911-1912, an increase of 25 per cent. In these two years the exports of "Chemicals and Drugs" amounted, respectively, to \$4,968,000 and \$4,034,000, of which Canada's own products amounted, respectively, to \$1,447,000 and \$1,677,000.

In the following list are given the amounts exported of the more important home products of chemical or related industries.

EXPORTS	1911-1912	1912-1913
Calcium acetate	\$ 218,000	\$ 311,000
Calcium carbide	200,000	199,000
Lye	33,000	39,000
Phosphorus	91,000	63,000
Dyes	5,000	14,000
Chicle gum	17,000	
Hemlock bark extract	36,000	24,000
Hops		42,000
Senega root	74,000	143,000
Casin	38,000	15,000
All other drugs, etc.	965,000	991,000
Fertilizers	945,000	1,636,000
Cresote oil		74,000
Paints, etc. (total)	109,000	156,000
Mineral pigments	35,000	27,000
Varnishes		79,000
Explosives	188,000	101,000
Minerals and mineral products:		
Arenic	82,000	108,000
Asbestos	2,098,000	2,487,000
Corundum	131,000	196,000
Mica	258,000	319,000
Graphite	66,000	79,000

EXPORTS	1911-1912	1912-1913
Graphite products	\$ 27,000	\$ 52,000
Pyrites	110,000	7,000
Coke	66,000	269,000
Gypsum (crude)	423,000	439,000
Wood pulp (chemically treated)	1,588,000	2,101,000
Wood pulp (mechanically ground)	3,307,000	3,409,000
Press cake	659,000	1,075,000
Matches	11,000	1,000
Sugar and sugar products (total)	171,000	151,000
Maple sugar	110,000	104,000

## RECENT INCREASE IN PRODUCTION OF LIME NITROGEN

The following are interesting figures from the report in Carbid and Acetylene of a lecture on artificial fertilizer materials and their significance to agriculture, by Conrad Kubierschky, of Eisenach, before a recent meeting of the Society of German Chemists at Breslau.

The Cyanamid produced from the beginning of the industry is as follows:

Year	Tons
1906	500
1907	2,200
1908	8,300
1909	16,000
1910	30,300
1911	52,000
1912	95,000
1913	97,000 (estimated)
1914	208,000 (estimated)

The increase in production of fertilizer materials within the last few years is as follows:

	Years	Average annual per cent increase
Cyanamid	1907-1912	212.0
Norway salt-peter	1903-1911	170.0
Oceanian phosphate	1901-1911	28.0
Tunis phosphate	1901-1911	24.0
Florida phosphate	1901-1911	17.4
Potash	1901-1911	11.0
Ammonium sulfate	1901-1911	10.5
Potash	1891-1900	10.0
Thomas phosphate	1900-1910	7.5
Superphosphate	1900-1910	7.8
Crude phosphate	1901-1911	8.0
Chili salt-peter	1901-1911	6.8
Guano	1901-1911	3.7
Algerian phosphate	1901-1911	2.0

## FURTHER HYDRO-ELECTRIC POWER UNDERTAKINGS IN NORWAY

The exploitation of water-power in Norway has recently received a tremendous impetus; reports of new companies organized to control and develop water-power rights appear with unusual frequency. An account of this development and comment on its probable outcome form the subject of an editorial article in *Engineering* (London), 98 (1914), 18.

Among the most important projects is a large power-station with a capacity of some 50,000 horse-power which is being laid out at the Folla River, an auxiliary to the Surna, in the Surendal. It will be necessary to construct a tunnel 3 km. long through the Sande mountain, whereby a satisfactory fall will be obtained. The station will be located at a place with good harbor accommodation and sites for new industries. In the absence of a natural reservoir it will be necessary to construct a dam across a flat valley, between the steep mountains of the Trolldheimen, and the wall across the Folla Valley is to be 20 meters high. This large undertaking is controlled by the owner of the water-power of the Heane River, in the Southern Drøntheim district, which, duly exploited, will represent some 15,000 horse-power, and this, it is understood, will be applied to electric ore-smelting. At Folla there are large deposits of limestone which have been secured.

The building of another hydro-electric power-station has just been decided upon, the cost of exploitation and transmission amounting to about \$975,000. The power will be derived from the Höförs Falls, and will amount to some 25,000 horse-power, which is to be transmitted to the town of Risör, a distance of some thirty miles. The fact that the power can be utilized in an existing town, instead of works and dwellings having to be built in an entirely desolate country, as is the case with so many

large power-stations, means a very material saving. The Akershus district has just purchased the Raanaasfos Fall; the price for the waterfall is \$275,000.

The Arendal Water-Power Company, which is already in operation, is to be greatly extended, at an outlay of some \$1,200,000, and the Bjølvo waterfall is to be exploited.

A Norwegian journal of some standing has recently given expression to some apprehension as regards an over-production of hydro-electric power-stations, more especially as far as the electro-chemical industry is concerned. Only a few years ago it was difficult to find uses for capacities of 5000 to 10,000 horse-power in this industry, but such capacities no longer count for anything. Now the installations and projected schemes comprise capacities of 50,000 and 100,000, or even several hundred thousand horse-power, in Norway, Italy, Spain, Savoy, Canada, and even in Iceland. As far as Norway goes, not only are the installations already in operation at Rjukan, Tysse, Arendal, etc., being extended on a large scale, but schemes are being advanced at Sande, Matre, Tyin, Aura, Take, Lysefjord, Bølve, Højangen, Osa, Glomfjord, etc. If only half of the projects just enumerated are completed within the first few years, the question presents itself as to how all this power shall be applied.

It is a well known fact that the old electro-chemical products, aluminum, carbide, ferro-alloys, all have very limited areas of consumption, which no doubt grow every year, but even a small overproduction leads immediately to a decline of prices and to crises. Such have already arisen twice during the comparatively short span of fifteen to twenty years which has passed since these manufactures commenced, and experts are already prophesying a third crisis, with ruinous prices below the cost of production, as being near at hand. It will be remembered that during the former crisis at least two Norwegian carbide manufacturers had to stop; the losses were heavy, as the factories had to be sold for a song.

On the other hand, the opinion is often expressed that the new electro-technical nitrogen industries have an unlimited scope for the sale of their products. But this view must assuredly be accepted with considerable reserve. In the market for artificial fertilizers the consequences of overproduction are already felt. The quotation for Chili saltpeter has dropped from 10.50 marks in the beginning of March to 9.55 marks in the beginning of May, the market having been unable to receive the offered quantities of Chili saltpeter and artificial fertilizers. Nor does the position of sulfate of ammonia offer any encouragement, as German reports show. Also the demand for cyanide shows signs of falling off.

In addition to all this, new methods have been discovered by which nitrogenous fertilizers can be manufactured chemically, without the aid of electricity (as, for instance, the Haber system) so there seems every reason not to embark too light-heartedly on the wholesale exploitation of water-power.

#### HYDROGENATED FATS AS FOODSTUFFS

A series of experiments on fats hardened by hydrogenation (peanut oil, sesame oil and cottonseed oil) has been carried out by Professor Lehmann of the Institute of Hygiene of the University of Würzburg, to determine, first, the amounts of nickel present (from the hydrogenation in contact with nickel) and whether these amounts are harmful; second, whether the fats are easily assimilable. Analysis showed that the fats contained a maximum of 6 mg. and a minimum of a little less than 0.1 mg. per kilogram [*Chem. Ztg.*, 38 (1914), 708]. Since the author's previous experiments have shown that much larger amounts—at least 100 mg. per day—have never been known to be harmful to human beings, and that in animal experiments 6–10 mg. per kilogram of body weight have caused no ill effects, toxic action from this source in hydrogenated fats is not to be feared.

In animal experiments, too, the fats proved easily assimilable

and in household tests of from two to six months no unpleasant effects of any kind were observed.

#### AMMONIUM SULFATE AND SODIUM NITRATE IN 1913

The figures for the ammonium sulfate exports of Germany and England in the last two years were published in *This Journal*, 6 (1914), 597. The whole situation is commented on in *Engineering* (London), 97 (1914), 760. The international market for ammonium sulfate and Chili saltpeter was, in 1913, unfavorably influenced by the conditions of the preceding autumn. Although the spring of 1913 encouraged, on the whole, the use of fertilizers, the demand fell off in the latter part of the year, and more material remained finally stored than had been on hand at the beginning of this year. This is true both of ammonium sulfate and sodium nitrate and its substitutes. The world's production of ammonium sulfate is steadily on the increase, and had, in 1913, risen to 1,365,700 tons, against 1,214,400 tons in 1912. Germany leads in this production with 549,000 tons in 1913; the United Kingdom comes next with 420,000 tons; then follow the United States with 177,000 tons, and France with 75,400 tons. We take these figures, which do not include British India, from the report of the German Ammoniak Verkaufs-Vereinigung for 1913. As regards consumption the lead of Germany is still more striking, the figures being for 1913: Germany 460,000 tons, United States 335,000 tons, Japan 115,000 tons, England 97,000 tons. Thus German consumption is much higher, especially for agricultural purposes, than that of any other country; but the United States is rapidly following that country, both as regards production and demand. This is, of course, an important factor in the international market. One feels some doubt about the future of the nitrolim and the synthetic ammonia processes, considering that the recovery of ammonia from coal-gas, the demand for which is not likely to decrease, is becoming more and more perfect. The manufacture of synthetic ammonia passed into the practical stage last year; some 50,000 tons of nitrolim and about 30,000 tons of Nor saltpeter were supplied last year. But the experiments on the oxidation of nitrogen by long electric arcs, which seemed so promising, have been given up, and whether the other electric oxidation processes will be able to stand the competition of the old-established products seems doubtful, though the further development of electric-power application and distribution may turn the scale in favor of electric processes. The production of Chili saltpeter, for the first time almost since 1885, decreased last year from 2,552,770 tons in 1912 to 2,450,000 tons.

#### AMERICAN COKE

The United States Geological Survey reports that all records in American coke production were broken last year, the output of the twelve months having been 46,311,369 tons, valued at \$128,951,430. This was an increase over the 1912 output of 2,327,770 tons in quantity and \$17,146,317 in value.

#### LABOR CONDITIONS IN GERMANY

According to the *Reichsarbeitsblatt* the number of workmen applicants in Germany per hundred vacancies amounted in March last to 173, as against 218 in February, and 234 in January. The figure for March of last year was 168. The figures for the current year point to an improvement. The situation has slightly improved in the building trades, leading to better conditions in the brick and tile industries and in wood-working. The same could be said for the textile industry, although cotton-spinning and weaving firms complained of lack of orders. There was a slackening in the activity in coal and lignite mining, as also in that of the iron and steel industry and engineering, except in the case of special machinery. The electrical and chemical trades continued to be satisfactorily employed.



### A SUBSTITUTE FOR GALVANIZED IRON

It is a well known fact that the purer iron is, the less liable it is to pitting and corrosion, chemically pure iron being practically rustless. A new process, described in *Engineering* (London), 97 (1914), 828, has just been brought out, termed "ferro-zincing" or "ironizing," it turns this fact to account by coating the steel surface with almost pure iron, the only impurity of any significance being hydrogen. The addition of hydrogen is an advantage, for the reason that it makes the iron slightly more electro-positive to the underlying steel than it would otherwise be, so that it forms a better protective coating.

Another advantage of the coating of electrolytic iron is that the coating is homogeneous, and is not under unequal strain caused by mechanical operations such as drawing or hammering, and has not been subjected to any heat or mechanical treatment which of necessity causes impurities to be absorbed by the metal so treated.

It is found in practice that it is advantageous to coat the electrolytic iron surface with zinc, as a zinc coating with an intermediate layer of pure iron hydrogen alloy gives a greatly increased life to an ordinary steel tube or plate for the reasons already given.

The inventor of the process, Mr. S. Cowper-Coles, has granted a license to the British Mannesmann Tube Company for the protection of boiler tubes, and is applying the process to a number of other purposes.

### OPEN-HEARTH AND BESSEMER RAILS IN AMERICA

In *Engineering*, 84, 688, it was pointed out how the gradual working in of the good Bessemer ores in this country had led to the production of rails dangerously high in phosphorus. It was also then suggested that the future would see a considerable change over from Bessemer to open-hearth rails for this reason. Figures quoted at the time showed that, in 1905, of 3,375,929 tons of rails rolled in the United States, only 183,264 tons were of open-hearth steel, the remainder being Bessemer. The figures, recently available, for 1913 [*Loc. cit.*, 97 (1914), 786] are a confirmation of the forecast. Last year 3,502,780 tons of rails were rolled in the United States, of which no less than 2,527,710

tons were open-hearth, the Bessemer production having, of course, fallen off in proportion.

### COMBUSTION ON GOLD AND SILVER SURFACES

Among the papers presented or reported at the 51st Annual Meeting of the Institution of Gas Engineers at Liverpool, the proceedings of which are reported in full in the *Jour. Gas Lighting and Water Sup.*, 126 (1914), 879 ff., is one on "The Electrical Condition of Gold and Silver Surfaces during the Absorption of Gases and Their Catalytic Combustion," by H. Hartley. The results of the investigation (*loc. cit.*, p. 912) may be summarized in the following conclusions:

1—A gold surface acquires a negative charge during the catalytic combustion of gases in contact with it.

2—This electrical effect is probably antecedent to the actual combustion, and is primarily due to "occlusion" phenomena.

3—The metal becomes negatively charged during the occlusion of the combustible gas (hydrogen or carbon monoxide), and positively charged during the occlusion of oxygen.

4—Such electrical effects are probably due to occluded gas which is leaving (rather than entering) the metal. Any cause, such as a sudden lowering of temperature, or a sudden increase in pressure, which would momentarily check the outflow of occluded gas, will likewise diminish the intensity of the charge, or may even momentarily stop it altogether. Conversely, a sudden diminution in the outside gaseous pressure in the vicinity of the metal, which would increase the rate of outflow of the occluded gas from the metal, will temporarily increase the intensity of the electrical effect.

5—Such temporary disturbances in the intensities of the electrical effects as are described in (4) are probably due to the fact that a change in either temperature or pressure of the system is accompanied by a change in the dynamic equilibrium between the in-going and out-flowing gas at the surface system, which change lags behind the exciting cause.

The investigation of the subject is being extended to other surfaces by Professor Bone, in the new Department of Chemical Technology at the Imperial College of Science and Technology, London.

## NOTES AND CORRESPONDENCE

### RELATION OF COMPOSITION OF ASH IN COAL TO ITS FUSING TEMPERATURE

*Editor of the Journal of Industrial and Engineering Chemistry:*

Your April number contains an article by Mr. Oscar W. Palmenberg on "The Relation of Composition of Ash in Coal to Its Fusing Temperature." The Engineering Department of the Crucible Steel Company has had this subject under consideration for some time, and has made some investigations, but as they are not yet so numerous as Mr. Palmenberg's, we are glad to get the information contained in his article and have given it a great deal of study, but draw somewhat different conclusions.

The substance of the article may be best stated by quoting the two following extracts:

"To show that there is no relation between the clinkering quality of a coal and the sulfur or iron content, the writer has made this investigation."

"Therefore a chemical analysis is of no value to arrive at a conclusion regarding the clinkering quality of a coal. It may be noted that although coals having an ash with a very low iron content seem to give the highest fusing ash, no definite fusing temperature fits a definite percentage and when the iron content goes beyond 10 per cent the fusing temperature cannot be judged at all. That the sulfur content of the coal has no

bearing whatsoever upon the fusibility of the ash is also apparent."

The two accompanying charts have been prepared from Mr. Palmenberg's tables, and an examination of them will show at least that there is reason for questioning the finality of his conclusions.

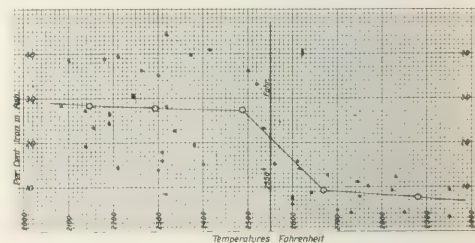


CHART I

CHART I—In Chart I the abscissae are based on the temperature Fahrenheit at which the ash fused, and the ordinates on the iron content. This chart shows that an ash containing less than 10 per cent of iron does not fuse at a temperature lower than 2550° F., and that when the iron content exceeds 20 per cent

the fusing temperature is never higher than  $2550^{\circ}\text{F}$ . Between 10 per cent and 20 per cent of iron the fusing temperature varies over a wide range.

A chart based on the sulfur content of the coal was made from the same tables and was found to give identically the same results as stated above, substituting 1 per cent and 2 per cent of sulfur content for 10 per cent and 20 per cent of iron. There were no exceptions. This chart is not reproduced.

CHART II goes a step further and shows a combination made by adding the sulfur to the iron—having first reduced the iron to its percentage as referred to the coal instead of to the ash. From

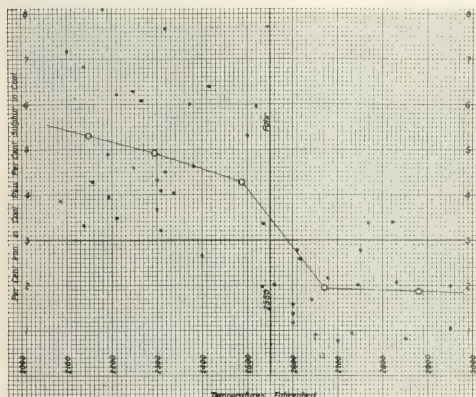


CHART II

this it will be noticed that under 3 per cent of sulfur plus iron the fusing temperature is above  $2550^{\circ}\text{F}$ , and over 3 per cent it is below that point. To this there are only three exceptions out of forty-five observations; and all three lie close to the 3 per cent line.

It is true, as Mr. Palmenberg says, that "no definite fusing temperature fits a definite percentage," but if the correctness of Chart II is not successfully attacked, it has considerable value, inasmuch as it indicates that the ash of coals containing more than 3 per cent of sulfur plus iron will fuse at a temperature less than  $2550^{\circ}\text{F}$ . This is a point below which it may be said in general that it is undesirable, and—with even moderately hard driving—impossible to keep the heat of a boiler furnace.

JOHN H. K. BURGWIN

PITTSBURGH, May 29, 1914

## THE EFFECTS OF THE ENSILAGE PROCESS ON THE SOLUBILITY AND METABOLISM OF FLOATS

The letter by E. B. Forbes, published in THIS JOURNAL, 6, 605, contains a statement which we find difficult to reconcile with the idea gained by us from a careful perusal of his original article. Mr. Forbes says, "In order to correct an impression given by Professor Mooers' article we would state that our especial interest in the subject was as applying to animal feeding. . . ." The opening paragraphs, however, of their original article read as follows: "One of the standard methods of adding floats to the soil is through its addition to manure, and the effect of the fermentation of manure on the solubility of floats has been the subject of discussion and experiment."

"It has occurred to the writers that perhaps we might profitably add a part of the floats to the plant-food two steps further from the soil by introducing it into the silo with the fodder corn, thus gaining two opportunities for increasing the solubility of the floats, first in the ensilage process, and second in the digestive tract of the animal; and further, giving to the animal such

benefit as it might be able to get from the rock phosphate in its passage through the body. We do not mean to suggest, however, that all of the floats which one might desire to add to the soil could in this way be passed through the silo and the animal."

These paragraphs are the only ones preceding the experimental data and the reader can easily come to an opinion as to whether or not we were justified in the impression that the main object was plant-food rather than animal feeding. Furthermore, while data were presented as to the effect of the ensilage process upon the solubility of rock phosphate no data were given by them in regard to the acceptance of livestock of treated ensilage as food.

We stand corrected for overlooking the composition of the phosphate rock, the total phosphorus in which we find reported in the article by Forbes and Fritz.

Mr. Forbes continues, "We do not follow . . ." the "conclusion that in the process of animal digestion there was reversion of the  $\text{P}_2\text{O}_5$  made soluble by the ensilage process." Our position was briefly this: if all the phosphorus eaten was voided in the dung then the relative availability of the phosphate which had passed through the animal could be determined by means of a weak acid solvent. As the availability when determined in this way proved decidedly less than that obtained by Forbes and Fritz in their ensilage work, we stated that reversion during the process of digestion was "indicated" and by no means did we draw the conclusion that such was certainly the case. Far more extensive investigations would be required in order to get conclusive evidence.

In regard to another part of our work, Mr. Forbes states, "It is also assumed that the rations involved in the comparison differed only in regard to the presence of rock phosphate, but the data submitted show marked differences in the proportionate amounts of the other components." The table shows that the animals of each group were given the same amount of cotton-seed meal and that there were placed before them the amounts of ensilage that they had in a preliminary trial been found to eat without waste. The amounts were practically the same for each group per 1000 pounds of live weight. Of course the refusal of the animals to eat all of the phosphated silage was unavoidable, and might give rise to minor differences in the analytical results. However, with the marked differences—amounting to more than 500 per cent on the average—between the  $\text{P}_2\text{O}_5$  content of the manure from the animals fed plain ensilage and those fed phosphated ensilage no great error would be expected. Further proof of this is supplied by the facts that the increase of the soluble  $\text{P}_2\text{O}_5$  per 100 pounds of rock phosphate was calculated to be 1.17 lb. for the heifer, which ate about 84 per cent of her full silage ration, and 0.93 lb. for the cow, which ate only about 61 per cent of her silage ration.

In conclusion, Mr. Forbes asks this question, "Is it not more likely that the cows absorbed and assimilated the soluble phosphate than that it 'reverted'?"

In reply we would say that since both of the animals which ate the phosphated ensilage lost in weight—as was shown in a table of our article—we considered the probability to be against the retention of any of the added phosphate.

C. A. MOOERS

DEPARTMENT OF CHEMISTRY AND AGRONOMY  
TENNESSEE AGRICULTURAL EXPERIMENT STATION  
KNOXVILLE, July 13, 1914

## ON ANALYSIS OF COPPER, TIN AND SILICON ALLOYS

We recently had occasion to analyze several alloys of copper, tin and silicon, and found that the usual methods of procedure would not answer. The reasons were quite obvious, and besides the alloys were insoluble in nitric acid. The following scheme of procedure was worked out and found to give entirely satisfactory results. The method is given in detail below. No

claim is made for originality other than adaptation to the work in hand:

**SILICON**—Weigh out 0.5 gram of alloy into a 400 cc. Erlenmeyer flask and cover with 20 cc. of water; add 15 cc. HCl and 5 cc.  $\text{HNO}_3$ . Boil until completely decomposed. Carefully add 20 cc. concentrated  $\text{H}_2\text{SO}_4$  and boil until sulfuric anhydride fumes are freely evolved. The silica is now completely separated and is dehydrated. Cool and carefully add 75 cc. of water. Boil until all sulfates are in solution and filter, catching the filtrate in a 200 cc. volumetric flask. Wash with hot water nearly to mark and place the flask in ice-water to cool, being careful to have the contents near the temperature of calibration of the flask, when it is finally made to the mark. Ignite, weigh the residue as  $\text{SiO}_2$  and calculate to silicon.

**TIN**—When the flask has cooled make up to the mark with water, and transfer 100 cc. to a 400 cc. Erlenmeyer flask, add 0.15 gram of finely powdered metallic antimony, dissolved in 5 cc. concentrated  $\text{H}_2\text{SO}_4$ , 35 cc. of concentrated HCl, and 1 gram of iron filings. Boil until the iron is nearly all in solution and then connect the flask by means of a three-hole rubber stopper which carries a right angle tube dipping into the liquid, to a carbon dioxide generator. The second hole in the stopper is fitted with an exit tube which connects to a small flask holding a saturated solution of sodium bicarbonate which acts as a seal. The third hole is fitted with a glass plug and serves to admit the burette tip during titration. The flask is now heated to boiling while  $\text{CO}_2$  is passing until all iron is in solution and reduction is complete: 20 to 30 minutes are usually sufficient. The flask is now removed from the flame and set in cold water to cool as rapidly as possible. The glass plug is now removed, a small funnel inserted, about 5 cc. starch solution poured in, and the plug replaced. When the contents of the flask are below  $40^\circ\text{C}$ ., the generator is shut off, the flask detached, and the tin rapidly titrated with  $\text{N}/10$  iodine solution which has been standardized against pure tin. Air must not enter the flask and the flask with the bicarbonate seal remains in place during the titration.

**COPPER**—The other 100 cc. portion is made alkaline with ammonia, then acid with nitric acid and allowed to digest on the hot plate for an hour. The stannic acid, which should now be white, is filtered off and washed well. To the filtrate 5 cc.  $\text{H}_2\text{SO}_4$  are added and it is boiled down to fumes, cooled, diluted with water, neutralized with ammonia, made acid with 7 cc. of a mixture of 2 parts 50 per cent nitric acid and one part 50 per cent sulfuric acid, washed into a 150 cc. beaker and the copper determined by electrolysis.

E. D. KOEPPING

THE ELECTRIC SMELTING AND ALUMINUM CO.  
LOCKPORT, N. Y., May 9, 1914

## ON THE RAPID DETERMINATION OF COPPER IN OPEN HEARTH AND ALLOY STEEL OR IN CAST IRON

The prevailing method of determining copper in steel by precipitation with hydrogen sulfide with subsequent incineration in porcelain, digestion with nitric acid and transfer of the solution to platinum, where it is again evaporated with hydrofluoric and sulfuric acids to remove silica, and re-solution in sulfuric acid is tedious and becomes even more so in the presence of molybdenum.

The following modification of Low's method will be found to give entire satisfaction, and is much more rapid and convenient where many samples are to be run than the well known method outlined above or any modification which involves electrolysis.

**METHOD** From 3 to 10 grams of steel are dissolved in 35 cc. of 1:1 HCl or 1:5  $\text{H}_2\text{SO}_4$  and then diluted with 35 cc. of water. A strip of sheet aluminum,<sup>1</sup> with the corners

<sup>1</sup> The use of cast pieces is to be avoided as they usually contain some copper.

bent up so that it will not lie flat on the bottom of the beaker, is then dropped in and the solution boiled vigorously for 20 minutes.

Remove from the hot plate and wash down the cover glass and the sides of the beaker with hot water. Filter through a 11 cm. S. & S. filter and wash thoroughly with hot water. Puncture the filter and wash the precipitated copper into a 300 cc. Erlenmeyer flask. Over the strip of aluminum in the beaker pour 3 cc.  $\text{HNO}_3$  and 7 cc. water, warm and pour through the paper, giving the beaker and paper a final wash with hot water.

The volume of the solution in the beaker should now be about 30 cc. Boil 15 minutes to remove any nitrous fumes. Add 7 cc.  $\text{NH}_4\text{OH}$  and boil until the deep blue fades to a very light blue and the odor of ammonia is faint. Add 10 cc. of 80 per cent acetic acid and boil one minute. Cool, add 10 cc. of 30 per cent KI solution and titrate with standard thiosulfate solution, using starch indicator.

**THIOSULFATE SOLUTION**—About 5 grams of the pure crystallized salt to one liter of water gives a solution, 1 cc. of which = 0.00125 gram of copper, approximately.

The solution should be standardized against a bichromate solution of known iron value, or against pure copper foil or a standard copper solution, the copper content of which has been accurately determined by electrolysis. A better method than any of the foregoing, to the writer's mind, is the use of a standard steel from the Bureau of Standards.

**STARCH INDICATOR**—The starch solution is prepared by allowing raw starch to soak in 0.1 per cent hydrochloric acid for 24 hours. The acid is then poured off and the starch washed with cold water until free of acid. The starch is then dried at  $32^\circ$ , occasionally stirring to break up the pieces, and finally drying at  $100^\circ$  for several hours. One gram of the starch prepared in this way boiled in 100 cc. of water and filtered will give a clear solution which will keep indefinitely and will give a brilliant transparent blue.

E. D. KOEPPING

ELECTRIC SMELTING AND ALUMINUM CO.  
LOCKPORT, N. Y., May 9, 1914

## TIN PLATE AND STEEL MILL OPERATIONS IN JULY

During July the tin plate mills ran at between 85 and 90% of capacity, one or two interests being to about 50%, while the others ran full. The Jones and Laughlin Steel Company operated thirty-two tin mills at its Woodlawn, Pa., plant having added eight mills to this plant in the record period of two months. The Woodlawn plant is now the largest in the United States, having during the week of July 13th wrested the honor from the Shenango plant at New Castle, Pa., which held first place for more than fifteen years. The third largest plant is the American, at Elwood, Ind., with twenty-eight mills, while the fourth in output is the National at Monessen, Pa., with twenty-five mills.

In July, steel mill operations in the Pittsburgh District averaged between 65 and 70% of the full capacity, while the average for the country at large was close to 65% of capacity. The production is somewhat larger than in the late part of May and this showing is looked upon as a favorable one by experts because ordinarily the production is much reduced in July. A slight improvement was noted in the demand for wire products.

W. A. HAMOR

## PLATINUM IN WESTPHALIA

A report of a general meeting of the Deutscher Platinwerke, held recently in Düsseldorf, given in the London *Mining Journal*, says that a platinum ingot of about 500 grams, obtained from the ore occurrences near Wenden in Westphalia, was shown. Dr. W. Hommel, of the Clausthal Mining Academy, made an interesting report on the ore deposits, in which he laid stress on the statement that the metal occurs with lead, zinc, antimony and nickel.

<sup>1</sup> *Chem. Abs.*, 4, 2617.



A sensation was caused when Dr. Hommel exhibited a lump of pure platinum, which was obtained, he stated, by smelting 1 ton of concentrates obtained from 25 tons of crude ore. In addition to the platinum, the concentrates gave about 10 to 12 per cent nickel. The cost of production including mining would be about \$4.76 per ton, and ores containing no more than 5 grams platinum would be payable.

#### CHEAPER PIG IRON

The Interstate Commerce Commission handed down on July 7th a decision of great importance to the pig iron business of the country.

The decision put into effect a substantial reduction on the freight rates on pig iron from Alabama, Tennessee and other Southern points to all Northern and Eastern consuming points. This will enable the Southern producers to effectively compete with the big pig iron producers of Ohio, Pennsylvania, Michigan

and Illinois. In substance the commission has cut the rate approximately 35 cents a ton on all rail and something like 45 cents on rail and water hauls. The commission's order goes into effect on October 1st, 1914.

The protestants stated that the decision would force a general readjustment of prices on pig iron. Ohio and Pennsylvania furnace operators will be compelled to cut the price of their product in order to meet the new competition.

The decision was handed down on a complaint brought by the Sloss-Sheffield Steel and Iron Company and others in the Birmingham and Tennessee districts. After it was filed, foundries and other users of Southern pig iron located in the North, East and West intervened on behalf of the complainants. Furnace operators in Ohio, Pennsylvania, Illinois, Michigan, Wisconsin and Minnesota made an organized effort to have the present rates maintained. The case has been pending for more than a year and the commission made an exhaustive investigation.

W. A. HAMOR

## PERSONAL NOTES

Dr. Arthur H. Elliott received the honorary degree of Master of Science on the occasion of the 50th anniversary of the founding of the School of Mines, Columbia University, May 29th. Dr. Elliott is at present abroad and is representing the American Gas Institute at various gas association meetings advancing the interests of the International Gas Congress.

Dr. Edward Dyer Peters, Gordon McKay Professor of Metallurgy at Harvard University, has received the honorary degree of Doctor in Engineering from the Royal School of Mines, Freiberg, Saxony. The degree was conferred upon Professor Peters in recognition of his academic and practical services and writings on the metallurgy of copper.

A license agreement has been made between the Pittsburgh Iron and Steel Foundry Company of Midland, Pa., and the United Engineering and Foundry Company of Pittsburgh, Pa., by which the latter concern will be permitted to manufacture "adamite" steel rolls for rolling mills. "Adamite" is a patented alloy which has been owned by the former corporation for several years.

At its recent commencement Wesleyan University conferred the degree of Doctor of Science on Dr. Walter P. Bradley, who has this year retired from the professorship of chemistry which he had held since 1893.

Dr. Jokichi Takamine entertained, on July 8th at the Nippon Club, a number of friends at a Japanese dinner given in honor of Dr. L. H. Backeland on the eve of his departure for Japan. Dr. Takamine officiated as toastmaster. Ellwood Hendrick directed to the guest of honor a characteristic and brilliant poem on the catalysis of friendship and good fellowship. The other speakers at the dinner were Charles F. McKenna, Charles Baskerville, Dr. H. Noguchi, M. C. Whitaker and H. S. May.

The U. S. District Court at Buffalo, Judge Hazel presiding, sustained Patent No. 939,757 of the Williams Patent Crusher & Pulverizer Co., in their suit against the Kinsey Manufacturing Co.

Dr. Hans Goldschmidt, the inventor of the Thermit Process and President of the Goldschmidt Thermit Co., is now paying his annual visit to the United States in order to keep in touch with his numerous interests in this country.

Dr. William L. Dudley, Dean of the Medical Department and Director of the chemical laboratories of Vanderbilt University, Nashville, Tenn., had conferred upon him the degree of LL.D. by the University of Cincinnati at its recent commencement.

The Pittsburgh Iron and Steel Foundry Company is erecting additional open-hearth furnaces and plans to make other important extensions to their plant at Midland, Pa.

Dr. Jerome Alexander is convalescing from a serious illness which has confined him to his home for the past two months.

Keuffel & Esser announce the removal of their Chicago headquarters to a new seven-story building which they have purchased, at 516-520 South Dearborn Street, Chicago. The main portion of the building, which is centrally located near the Buren "loop" between Van Buren and Harrison Streets, will be occupied by their stockrooms and offices.

Dr. Ross A. Gortner, since 1909 resident investigator in biological chemistry at the station for experimental evolution of the Carnegie Institution of Washington, has been appointed associate professor of soil chemistry in the University of Minnesota.

President Francis P. Venable has retired from the presidency of the University of North Carolina and has assumed the chair of the Francis Preston Venable Professorship of Chemistry in the University of North Carolina.

The Tagliabue Manufacturing Company have announced the issue of a Codex giving full information about industrial thermometers.

Ralph W. Perry, Ph.B. announces that he has severed his connection with the Michigan Central Railroad as Chemist and Engineer of Tests, in which capacity he has served them during the construction of the Detroit River Tunnel, the New Station and subsequent improvements to their terminal in the City of Detroit. Mr. Perry has leased the laboratory used in the above work for a general Chemical, Inspecting and Testing business to be known as the "Perry Testing Laboratory."

Professor J. Miller Thomson, F.R.S., is retiring at the end of this session from his position as Vice-principal of King's College, London and head of the chemical department of the college, after a service of forty-three years.

J. U. N. Dorr was given the honorary degree of Mining Engineer at the recent commencement of Rutgers College, New Brunswick, N. J., in recognition of his contributions to gold and silver metallurgy.

Archibald F. Law, Vice-President and General Manager of the Temple Iron Company, which controls furnaces at Temple, Pa., died at Scranton, Pa., on July 19, 1914, aged 58 years. Mr. Law's grandfather, Charles Law, introduced underground (shaft) mining in Pennsylvania.

Mr. C. M. Means, Electrical Engineer, of Pittsburgh, Pa., has been appointed Consulting Electrical Engineer with the U. S. Bureau of Mines.

Mr. Wm. W. Clark has resigned as Chief Chemist for the American Vanadium Co., and has accepted the position of Metallurgist with the Seymour Manufacturing Co., Seymour, Conn.

Joseph Soisson, aged 85, the pioneer manufacturer of firebrick used in the construction of coke ovens, died at his home in Connellsville, Pa., on July 19, 1914. Mr. Soisson began the manufacture of firebrick sixty-five years ago, and at the time of his death was the president of the Soisson Fire Brick Company.

The manufacturing plant of the Leicester Rubber Co., at Catasauqua, Pa., was totally destroyed by fire on July 19, 1914,

with a loss of \$75,000. The principal stockholders of the company reside at Trenton, N. J.

Plans are maturing at Sebring, Ohio, for the erection of a new pottery plant. There are five potteries in operation there now, having a combined capacity of 42 kilns. The new pottery will be of either six or nine kilns, and will add about \$12,000 to the monthly pay-roll of Sebring.

## GOVERNMENT PUBLICATIONS

By R. S. McBRIDE, Bureau of Standards, Washington

**NOTICE**—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate. Consular Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington. The regular subscription rate for these Consular Reports mailed daily is \$2.50 per year, payable in advance, to the Superintendent of Documents.

### HOUSE OF REPRESENTATIVES

**Utilization of Alaskan Coal.** The Naval appropriation act of Aug. 22, 1912, provided for a survey and testing of coal from the Alaskan fields with a view to its availability for use by the ships of the U. S. Navy. The report resulting has been printed as House document 876, 63rd Congress. It is unfavorable to the use of Alaskan coal under existing conditions. The elaborate report fills a pamphlet of 123 pages illustrated by many plates and maps.

### PUBLIC HEALTH SERVICE

**The Pollution of Tidal Water.** By HUGH S. CUMMING. Reprint 181 from the Public Health Reports. This is an address given before the Maryland Conservation Association, February 25, 1914. It discusses the bearing of tidal water pollution upon health and the importance to the State of its control. The subject is developed primarily from the hygienic standpoint, but is of interest also in connection with sewage disposal, water supply, and the shell-fish industry.

### DEPARTMENT OF AGRICULTURE

**Identification of Commercial Fertilizer Materials.** By WILLIAM H. FRY. Department Bulletin 97. 13 pages. Paper, 5 cents. This bulletin, which is contributed from the Bureau of Soils, "gives methods for identifying the carriers of the various fertilizing ingredients, and is intended to serve as a laboratory guide to those studying this phase of the fertilizer question."

**Arsenate of Lead as an Insecticide against the Tobacco Horn-worms in the Dark-Tobacco District.** By A. C. MORGAN and D. C. PARMAN. Farmers' Bulletin 595. 8 pages. This bulletin from the Bureau of Entomology is primarily of interest in the tobacco growing industry of Kentucky and Tennessee. It indicates, however, a probable outlet for the chemical product suggested.

**Economic Waste from Soil Erosion.** By R. O. E. DAVIS. Separate 624. 18 pages. 5 cuts. This pamphlet is an excerpt from the 1913 yearbook; it is a contribution from the Bureau of Soils.

**Hemp.** By Lyster H. Dewey. Separate 628. 63 pages. 15 cents. This excerpt from the 1913 yearbook gives an extended report which is developed largely from the standpoint of the fiber-plant investigator.

### BUREAU OF FISHERIES

**Fishery Industries.** By FRED M. CHAMBERLAIN and WARD T. BOWER. This article is included as one of the special papers in the report of the commissioner of fisheries for the year ending

June 30, 1913. It is of interest as giving a general summary of this industry.

### BUREAU OF FOREIGN AND DOMESTIC COMMERCE

**Cottonseed Products and their Competitors in Northern Europe.** By ERWIN W. THOMPSON. Special Agents' Series 84. 93 pages. Paper, 10 cents. Part 1 of this report is already issued; it deals with cake and meal. Part 2, which is to follow shortly, will deal with oils.

**Utilization of Potatoes in Europe.** By ROBERT P. SKINNER and other Consular Officers. Special Consular Report 64. 44 pages. 10 cents. This report is of interest in connection with the starch and alcohol industries as the statistics given indicate the consumption of potatoes in the various European districts not only as food and feeding material, but also in their industrial application.

### BUREAU OF STANDARDS

**Standard Analyzed Samples—General Information.** Supplement to accompany Circular 25. 5 pages. In this pamphlet are given the certificate analyses for the standard samples of iron, steel, ores, calorimetric materials, etc., which are issued by the Bureau of Standards.

**United States Specification for Portland Cement.** Second edition of Circular No. 33. 28 pages. The revised edition of this Circular includes only minor changes and additions from the 1st edition which was issued in July, 1913.

**Flame Standards in Photometry.** By E. B. ROSA and E. C. CRITTENDEN. Scientific Paper 222. 40 pages. This paper is a revision of one published in 1910 (Transactions of the Illuminating Engineering Society, 5, 753-78), entitled Report of Progress on Flame Standards. Further experiments are reported, but these have not materially changed the conclusions previously stated and many of the tables stand as in the original. The effect of atmospheric conditions upon several types of standard lamp is fully discussed and certain suggestions made as to the development of a primary standard for photometry.

**Special Studies in Electrolysis Mitigation.—No. 2. Electrolysis from Electric Railway Currents and Its Prevention; an Experimental Test on a System of Insulated Negative Feeders in St. Louis.** By E. B. ROSA, BURTON MCCOLLUM and K. H. LOGAN. Technologic Paper 32. 34 pages. This paper gives experimental data obtained during the practical working out of a system in St. Louis. In general no chemical factors are considered, the problem being treated from the electrical engineering viewpoint.

**Combustion Method for the Direct Determination of Rubber.** By L. G. WESSON. Technologic Paper 35. 11 pages. This paper was printed in full in THIS JOURNAL, 6, pages 459-62.

### GEOLOGICAL SURVEY

**Useful Minerals of the United States.** Compiled by SAMUEL SANFORD and RALPH W. STONE. Bulletin 585. 250 pages. Paper, 20 cents. This bulletin contains first, a list of the occurrences for all commercially important deposits of minerals arranged alphabetically under each State; second, a glossary of over 400 names. This glossary includes in addition to the definitions, a list of the states in which the mineral occurs; it is, therefore, virtually an index to the first part. A general

statement of the occurrences of the minerals is given with the idea of making this publication useful to the manufacturer, miner, or student of economic conditions rather than to the professional mineralogist. The more extensive deposits of some common mineral products such as clay, coal, and iron ore are mentioned only in general terms. This is the first publication of the Government giving a general summary of the mineral resources since 1887. However, Geological Survey Bulletin 507, "The Mining Districts of the Western United States," and one chapter of the 1912, "Mineral Resources," give limited information of similar character and these two sources are of interest in connection with the present bulletin.

**Production of Copper in the United States in 1913.** By B. S. BUTLER. This advance statement gives the first full summary of statistics prepared for the comprehensive report on the copper industry. The full report will be published later by the Geological Survey as a part of the general review of the industries of gold, silver, lead, zinc, and copper. The following data appear in this advance statement:

PRODUCTION OF PRIMARY COPPER IN 1913			
	Domestic		Foreign
Primary production:			
Electrolytic.....	1,022,497,601		378,243,869
Lake.....	155,715,286		
Casting.....	22,606,040		
Pig.....	36,004,986		
	1,236,823,913		378,243,869
Total primary.....		1,615,067,782	
Secondary production:			
Electrolytic.....		14,862,577	
Casting.....		22,360,182	
Total secondary.....		37,222,759	
Total output.....		1,652,290,541 lbs.	

From the above statistics and the stock of copper on hand at the beginning and end of the year and the export of copper, the apparent consumption of new refined copper and secondary copper and copper in alloys is found to be 1,085,000,000 pounds.

#### SUPERVISING ARCHITECT, TREASURY DEPARTMENT

**Specification for Lubricating Oils.** As a part of the information given to bidders proposing to furnish cylinder, engine, and motor oils for use in buildings under the control of the Treasury Department the following specification is included:

"Quality—The oils furnished must be of a suitable quality to give proper lubrication without the use of excessive quantities. They must be free from mineral acids and must not contain such an amount of organic acid as to indicate improper refining or inferior stock. Cylinder oil must flow at a temperature of 50° F. The custodian of the building for which the oil is ordered shall be the judge as to whether it gives proper lubrication."

#### CONSULAR REPORTS, JUNE

Large soap factories are in operation in Hong-Kong and Shanghai, using cocoanut oil from Manila, soda from Germany and Great Britain, and rosin from the United States. (P. 1212.)

**Asphalt-paper pipes** are being used in Austria as it is claimed that they can replace clay and iron pipes for most purposes. (P. 1213.)

**Petroleum** has been struck in Venezuela, on the eastern coast of Lake Maracaibo. (P. 1214.)

The magnesite deposits of Greece are mostly found in serpentine rocks. Much of it is calcined directly at the mines; large amounts of **magnesia** and **magnesite brick** are exported from Greece to the United States, where the only commercial supply is located in California. (P. 1239-41.)

**Soap makers** of Venezuela are endeavoring to have the import duty on cottonseed oil reduced, so that this oil can be profitably used. (P. 1255.)

A very active **radium** spring has been discovered at Gollitz, Bohemia. (P. 1257.)

The International Association of Silk Dyers at Lyons, France, has increased the price of **dyeing silk** owing to increase in cost

of materials and labor. No responsibility is assumed for dyeing previously weighted silks. (Pp. 1258-9.)

A German inventor, Johannes Marschall, has patented a furnace containing a series of thermopiles, from which he claims to produce **electricity** directly from coal at a cost below regular practice. (P. 1278.)

The Greek government has just signed a contract with the Standard Oil Company of New York for 93,000 cases of **petroleum** oil. (P. 1294.)

The Belgian **cement industry**, especially exports, shows a decline. (P. 1295.)

A new **plate glass** factory is to be established at Jorda, Hungary, using **natural gas**. (P. 1359.)

The production and use of **kelp** in the United Kingdom for **fertilizer** and for **iodine** are described. (Pp. 1402-5.)

A large **beet-sugar** factory is to be built at Winnipeg, Canada. (P. 1409.)

**Asphalt** of good quality has been discovered in the Philippines. (P. 1422.)

A factory for **briquetting** slack coal is to be erected at Nanaimo, near Victoria, Canada. (P. 1426.)

Statistics of the World's production of **raw silk** are given. (P. 1434.)

The mineral products of the Philippine Islands include **iron**, **silver**, **gold**, **coal**, **clay products**, **lime**, **sand**, **stone**, **salt**, and **mineral water**. (P. 1456.)

The **dry-milk industry** of Norway is in a transition stage, but soon new processes will be installed in which the milk will be dried as a film instead of by spraying. (Pp. 1480-1.)

**Methyl alcohol** to be used in the manufacture of **formaldehyde** is exempted from the manufacturing tax in Italy, if denatured by the addition of formaldehyde. (P. 1516.)

Birmingham, England, conducts four **municipal industries**, viz., **water**, **gas**, **electricity** and **street railways**. The average cost of gas for 1913 was given as 38.8 cents per 1000 cubic feet. (P. 1539.)

**Water hyacinth** is being investigated in Judo, China, as a source of fiber. This fiber has about the same quality as **jute**; it dyes readily and is strong. (P. 1543.)

The output of **mineral products** in Chili has increased, especially **sodium nitrate**, **copper**, **coal**, **borax** and **phosphate**. (P. 1582.)

A new **oil-bearing nut** has been found in the Philippines, from a tree supposed to belong to the genus *Amoora* or *Dysoxylum*. The nut contains 45 per cent of a new edible oil which has been found useful in the manufacture of **soap**, but not as a drying oil. (P. 1615.)

**Mills** in Judo, China, for the production of **paper pulp** from bamboo have not been very successful, but are being reorganized. (P. 1627.)

A new high-power **explosive**, **sabulite**, to be manufactured at Coquitlam, British Columbia, for blasting is claimed to be three times as efficient as **dynamite**, to be safe in handling, not to be effected by temperatures from -75° F. to +258° F., and to evolve no poisonous fumes on explosion. (P. 1641.)

A committee of experts has been appointed in Sweden to investigate the possibilities of the production of **mineral oil** and **sulfur** from Swedish deposits of "alum shale" or "alum slate" which is a mixture of **pyrite**, **aluminum silicate** and **bituminous matter**. (P. 1707.)

The Hong-Kong Exporters Association is endeavoring to establish **standards of quality** for their exports, especially **wood oil**, **cassia**, and **cassia oil**. (P. 1710.)

A cargo of Spanish **sugar-beet pulp** has been shipped to Boston and New Orleans for feeding cattle. (P. 1711.)

The **turpentine** industry in India is being increased. (P. 1712.)

The production of **petroleum** in the Caucasus has decreased in the last decade. (P. 1717.)



The **petroleum** output of Peru is largely used as **fuel oil**, especially in Diesel motors. (P. 1729.)

**By-product coke ovens**, mostly of the Coppe, Carway and Otto types, are largely replacing the bee-hive type in Russia. (Pp. 1732-3.)

The peppermint industry in Japan is increasing, the principal products being **peppermint oil** and **menthol**. (P. 1738.)

The statistics of the areas planted in **sugar beets** in Europe show an increase. (P. 1773.)

The conditions of the following industries in France are discussed, *viz.*, **brewing**, **phosphates**, **coal**, **iron and steel**, **artificial silk**, **sugar**, and **alcohol**. (Pp. 1841-5.)

Efforts are being made to develop a large **cottonseed-oil industry** in India, the second largest cotton-producing country in the world. (Pp. 1866-7.)

Experiments at Croydon, England, indicate that the addition of one seven-hundredths grain of **radium** per ton of soil, causes marked increase in the rate of plant growth. Radium residues may be used as the source of radium. (P. 1871.)

**Gunpowder** for the Swedish government is made in a government factory, the principal explosives used being **nitroglycerine**, and **nitrocellulose**, with smaller amounts of **trinitrotoluol**. (P. 1890.)

**Soya bean oil** is being refined in Germany to be used in the manufacture of **artificial butter** and **lard**, and as **salad oil**. (P. 1908.)

The manufacture of **aluminum ware** in India is increasing, and the possibility of producing the metal is being considered. (P. 1924.)

The oil of the **cohune nut** is in great demand in Europe as a hardening ingredient in **margarin**. Great difficulty is experienced in cracking the nuts by machine without damaging the kernels. (Pp. 1930-1.)

Discovery of **petroleum** in Calgary, Canada, has caused considerable prospecting. (P. 1957.)

The **sea-weed industry** of France includes its use for **fertilizer** and for the manufacture of **iodine** and **potash** (Pp. 1988-90.)

The **sisal** produced in Bahamas is mostly shipped to the United States. (P. 1994.)

Removal of the duty on **charcoal** has made possible the importation of charcoal from China to the United States. (P. 1997.)

Statistics and other **information regarding exports** from various localities to the **United States** will be found as follows:

Belfast—Fusel oil, hides, paper stock, tow, and whiskey. (P. 1209.)

Florence—Hemp, marble, porcelain, hides, raw silk, terra cotta, and wine. (P. 1285.)

Cuba—Hides, copper, molasses, sugar, wax, alcohol, and asphalt. (P. 1289.)

Rouen, France—Tanning liquor, fusel oil, rubber substitute, lubricating oil and paper stock. (P. 1308.)

Aleppo, Turkey—Gum tragacanth, licorice root, and hides. (P. 1334.)

Jaffa, Turkey—Hides, sesame seeds and oil, olive oil, and wines. (P. 1345.)

Smyrna—Chrome ore, emery, gum mastic, gum tragacanth, laurel, licorice root, olive and sesame oil, opium, and hides. (P. 1373.)

Singapore—Benzine, copra, cubes, gambier, gums, gutta jelutong, gutta percha, hides, spices, cocoanut oil, wood oil, patchouli leaves, rubber, stick lac, tin, and paraffin. (P. 1396.)

Valencia, Spain—Coal, mineral phosphate, and petroleum.

Moscow—Drugs, furs, hides, mineral oils, spirits, and wines. (P. 1466.)

Bombay—Beeswax. (P. 1468.)

Munich—Beer, chemicals, glue, metal, paper, pumice, rennet, scientific apparatus, and skins. (P. 1474.)

Hongkong—Aniseed oil, cassia and cassia oil, tin, and peanuts. (P. 1483 and 1786.)

Carlsbad—Beer, uranium, color, chemical glassware, glue, kaolin, lenses, lupuline, mineral water, rennet, mineral salts, artificial silk, and zinc oxide. (P. 1495.)

Prague and Reichenberg—Beer, potassium carbonate, barium chloride, zinc oxide, potassium permanganate, coffee substitute, gelatin, glue, graphite, paraffin, sod oil, and tool steel. (Pp. 1500-5.)

Calgary, Canada—Fertilizer, glycerine, hides, and oil cake. (P. 1511.)

Dundee and Aberdeen, Scotland—Flax, hemp, jute, gauge glass, paper stock, spirits, horn, and iron grit. (Pp. 1528-32.)

Leghorn and Carrara, Italy—Alabaster, argols, beeswax, boracic acid, glass bottles, glue stock, glycerine, hemp, hides, juniper berries, marble, mercury, olive oil, pumice stone, sienna, soap stock, talc, umber, and wine. (Pp. 1536-7.)

Valparaiso—Beeswax, coal, copper and copper ore, skins, gold, sodium nitrate, quillaja bark (soap bark), and silver. (P. 1589.)

Riga and Liban, Russia—Drugs, flax, hemp, glue stock, hides, linseed, mineral oil, rennet, wood pulp, fusel oil, and turpentine. (P. 1632.)

New Zealand—Hides and kauri gum. (P. 1647.)

Barcelona—Antimony oxide, argols, bones, cork, glycerine, licorice, olive oil, fusel oil, oleo stearin, saffron, sugar beet pulp, skins, mineral water, and wine. (P. 1658.)

Brunswick, Germany—Asphalt, paints, optical glass, scientific instruments, potash, quinine, and sugar. (P. 1670.)

Rosario, Argentina—Bones, hides, copper ore, linseed and quebracho. (P. 1686.)

Batum, Russia—Licorice, manganese ore, potassium carbonate, and hides. (P. 1717.)

Southampton—Scientific instruments, metals, skins, spirits, cocoa, drugs, gum, gutta percha, mica, and rubber. (Pp. 1728-9.)

Guayaquil, Ecuador—Gold, hides, ivory, nuts, kapok, and rubber. (P. 1755.)

Costa Rica—Gold, rubber, silver, and sugar. (P. 1759.)

Ontario—Artificial abrasive, beet pulp, beet sugar residue, bones, gold, silver, carbons, ammonia, arsenic, glycerine, cyanide, sulfuric acid, coal, coal tar, coke, diamonds, gas liquor, glue stock, grease, gum chicle, hides, lime juice, milk powder, feldspar, graphite, mica, silica, talc, cottonseed, creosote, fusel and petroleum oils, ores of cobalt, copper, nickel, corundum, gold, iron, pyrite, and silver; paper stock, rubber, flaxseed, soap stock, steel, tallow, tan bark, paraffin, and whiskey. (P. 1885.)

Stettin, Germany—Amber, cellulose, drugs, dextrin, ceramics, glycerine, palm oil, rapeseed oil, potash and wood pulp. (P. 1911.)

Newcastle-on-Tyne—Antimony, asphalt, barium carbonate, coal, coke, paint materials, copper matte, hides, ceramics, fluor spar, pig iron, silica ware, steel, and ammonium sulfate. (P. 1950.)

West Hartlepool, England—Diamond grit, ferromanganese, fertilizer, pig iron, linoleum, salt, slag blocks, spiegeleisen, and steel. (P. 1952.)

Uruguay—Bones, casein, fertilizer, glue stock, guano, and hides. (P. 1954.)

Nagasaki—Coal, graphite, and vegetable wax. (P. 1976.)

## BOOK REVIEWS

**Welding and Cutting of Metals: Oxyacetylene Process.** Published by the Vulcan Process Company, Minneapolis. 86 pages. Cloth-bound. Price, \$1.00.

This little book contains drawings and descriptions of the various appliances used in the oxyacetylene welding operations, together with a description of the methods of application. It also contains a number of illustrations of successful welds and tabular data covering the range of application. The book will be useful to anyone interested in construction and repair work coming within the range of this process.

M. C. WHITAKER

**The Synthetic Use of Metals in Organic Chemistry.** By ARTHUR J. HALE, B.Sc. (Lond.), A.I.C. Pp. xii + 169. P. Blakiston's Son & Co., Philadelphia. 1914. Price, \$1.50.

Many reactions and syntheses of organic chemistry in which metals and their compounds take part are presented in this book. The chapters include reactions involving sodium and potassium, copper and silver, magnesium, calcium and barium, zinc and mercury, aluminum, tin and lead, iron, nickel and platinum, followed by six appendices containing experiments exemplifying a number of the methods mentioned in the text.

This work is based upon a course of lectures to advanced students, and, to judge from the text, presupposes a rather thorough knowledge of elementary organic chemistry. The number of reactions taken up is surprisingly large for a book of this size. A detailed discussion of any one of them is therefore obviously impossible. The weakness of the presentation lies in the lack of a systematic classification of the material. A systematization of the reactions as a whole, at which at least an attempt might have been made, would have added greatly to the value of the book, especially in connection with reactions of inorganic chemistry. As a further result of the concise treatment, the student is left in doubt as to the value of the reactions from a practical standpoint except in the case of those for which experimental details are given in the appendices.

In a book of this nature, some slips are inevitable, but on the whole fewer are apparent than would ordinarily have been expected. Some of the reactions, such as the preparation of triphenyl methyl, etc., for example, might have been brought more up to date. While other minor criticisms might be made, this book should prove of value to those chemists who wish a summary of the reactions of organic chemistry in which metals or metallic compounds take part.

K. G. FALK

**Modern Steel Analysis. A Selection of Practical Methods for the Chemical Analysis of Steel.** By J. A. PICKARD, B.Sc., A.R.C.Sc., A.I.C., Carnegie Research Scholar of the Iron and Steel Institute, Fellow of the Chemical Society of London. Pp. viii + 128. Illustrated. 12mo. Cloth, \$1.25, post-paid. P. Blakiston's Son & Co., publishers, Philadelphia.

The author states in the Preface that he has "endeavored to condense into a small space practical methods for the exact estimation of all those constituents of steel which are of fairly common occurrence. No attempt has been made to give a comprehensive description of all the processes used in the analysis of steel, but the methods detailed have been selected for their practical utility.

The first section of the book is on General Procedure. This is an admirable feature of the book, wherein the author gives practical suggestions relative to weighing, precipitation, filtration, evaporation and baking, absolute value of results, arrangement of work, sampling, and useful apparatus. Under weighing

precipitates the following is given as an example of a very practical suggestion: "A good many precipitates, such as silica, barium sulfate, aluminum oxide, are most conveniently weighed by brushing out of the crucible, into the balance scoop, taking precautions against loss by performing the operation over smooth paper. \* \* \* \* \* This procedure is to be recommended not only on the ground of speed and convenience, but also for its accuracy."

Methods for the following elements in steel are given in their alphabetical order: Aluminum, Arsenic, Carbon, Chromium, Cobalt, Copper, Hydrogen, Manganese, Molybdenum, Nickel, Nitrogen, Oxygen, Phosphorus, Silicon, Sulfur, Titanium, Tungsten, Uranium and Vanadium. This is followed by Appendix I, Solutions; Appendix II, Analysis of Different Steels and Alloys.

The methods given are, in general, those in practice in iron and steel laboratories. We note with regret the absence of Dr. Drown's well-known method for the determination of silicon in steel; that "SiO<sub>2</sub> contains 46.93 per cent Si," and that the author uses the word "estimation" throughout the book as a heading before giving the method.

WILLIAM BRADY

**Underground Waters for Commercial Purposes.** By FRANK L. RECTOR. 98 pp. 8 figs. John Wiley & Sons, New York. 1913. Price, \$1.00.

The first thirty-one pages of this book reviews for us our "Physical Geography" lesson on "Water and Its Occurrence." We learn that, "... thermal springs and geysers exist in widely separated parts of the universe;" that, "its (water's) specific gravity is 1 at 15° C.," etc., etc. Then follow two very interesting chapters. The one, on "Watershed" (8 pages), more especially concerned with the relation of the watershed to epidemics; the other, on "Mineral Water" (9 pages), gives us ten definitions of the term by as many different authorities and cites various classifications of mineral waters. Just as we are becoming interested in "Underground Waters" we find that the author has grown weary of his task and has filled out his book with a compilation of analytical methods and tables. The analytical methods are given too briefly to be of assistance to the analyst and too technically for the lay reader.

A. M. BUSWELL

**Sugars and their Simple Derivatives.** By JOHN E. MACKENZIE. J. B. Lippincott Co., Philadelphia. 1914. xvi + 242 pp. Price, \$2.25, net.

This book is based on a course of lectures given by the author to a class of students, some in pure chemistry and others interested in medicine, brewing, distilling, the manufacture of sugar, etc. The more important physical and chemical properties of most of the simple carbohydrates are given, and considerable space is devoted to a description of methods for the determination of their structural formulae and stereochemical configurations. Special chapters on subjects like the manufacture of cane sugar, fermentation, and the metabolism of the sugars are presented in a brief way.

The form of the book does not lend itself very well to connected reading and it probably will be most used as a companion to works on physiological and analytical chemistry and brewing, where no very complete references on the subject are necessary.

Since E. F. Armstrong's "The Simple Carbohydrates and the Glucosides" has already appeared, there seems to be little reason why a second book so similar in character should have been published.

J. M. NELSON

# NEW PUBLICATIONS

By D. D. BEZOLZHEIMER, Librarian The Chemists' Club, New York

- Alumina, The Manufacture of.** By A. BEUGE. 8vo. 70 pp. Price, \$1.25. Wilhelm Knapp, Halle. (German.)
- Analysis, Blowpipe.** By NICHOLAS KNIGHT. 5th Ed. 8vo. Cornell College, Mt. Vernon, Iowa.
- Coke, Fundamentals of the Chemistry of.** By O. SIMMERBEACH. 2nd Ed. 1. 8vo. 314 pp. Price, \$2.50. Julius Springer, Berlin. (German.)
- Color Chemistry, Textbook of.** By HANS TH. BUCHHEIM. 8vo. 537 pp. Price, \$5.50. Otto Spamer, Leipzig. (German.)
- Constants, Selection of Physical.** By H. ABRAHAM AND P. SACERDOTE. 8vo. 753 pp. Gauthier-Villars, Paris. (French.)
- Copper, Metallurgy of.** By H. O. HOFMAN. 8vo. 556 pp. Price, \$5.00. McGraw-Hill Book Co. New York.
- Explosives, The Production of.** A. VOIGT. 8vo. Price, \$1.75. Wilhelm Knapp, Halle. (German.)
- Inorganic Chemistry, Fundamentals of.** By C. OPPENHEIMER. 8th Ed. 8vo. 246 pp. Price, \$0.90. G. Thieme, Leipzig. (German.)
- Invention and Imitation.** By RICHARD WIRTH. 8vo. 265 pp. Price, \$1.25. Julius Springer, Berlin. (German.)
- Matter, Study of the Conditions of.** By P. P. VON WEIMANN. Vol. 2. 8vo. Price, \$2.25. Theodor Steinkopff, Dresden. (German.)
- Nitrocelluloses, The.** By C. HAUSERMANN. 8vo. 34 pp. Friedrich Vieweg & Sohn, Brunswick. (German.)
- Nitrogen, The Fixation of Atmospheric.** By JOSEPH KNOX. 8vo. 110 pp. Price, \$0.50. Gurney and Jackson, London.
- Organic Chemistry, Principles of Analysis and Synthesis in.** By M. HANRIOT, P. CARRE, et al. 8vo. Ch. Dérangeur, Paris. (French.)
- Photographic Chemistry, Treatise on.** By L. MATHET. Vol. 2. 3rd Ed. 8vo. Price, \$4.00. G. Mendel, Paris. (French.)
- Photography, by Means of Artificial Light.** By A. LONDE. 18mo. Price, \$1.00. Doin et Fils, Paris. (French.)
- Physical Chemistry, A Manual of Practical.** By FRANCIS W. GRAY. 8vo. Macmillan Co., New York.
- Physical Chemistry, Textbook of Vol. I.** By KARL JELLINKE. Vol. 4. 1. 8vo. 732 pp. Price, \$6.75. Ferdinand Enke, Stuttgart. (German.)
- Steel Analysis, Modern.** By J. A. PICKARD. 8vo. J. & A. Churchill, London.
- Steel Foundry, The.** By JOHN HOWE HALL. 8vo. 271 pp. Price, \$3.00. McGraw-Hill Book Co., New York.
- Stereochemistry.** By E. WEDEKIND. 2nd Ed. 8vo. G. J. Gieschen, Berlin. (German.)
- Terpenes and Camphor.** By O. WALLACH. 2nd ed. 1. 8vo. 580 pp. Price, \$6.75. Veit & Co., Leipzig. (German.)
- Triphenylmethyl.** By J. SCHMIDLIN. 8vo. Price, \$2.20. Ferdinand Enke, Stuttgart. (German.)
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- Alkali, Electrolytic Production of, in Bell and Diaphragm Cells.** ANONYMOUS. *Chemical Engineering and the Works Chemist*, Vol. 4, 1914, No. 37, pp. 129-136.
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- Alloys, Nomenclature of Non-Ferrous.** By G. K. BURGESS AND C. P. KARR. *Transactions of the American Institute of Metals*, Vol. 7, 1913, pp. 141-160.
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- Fats, Hardening (Hydrogenating).** By A. BERGIUS. *Zeitschrift fuer angewandte Chemie*, Vol. 27/I, 1914, No. 46, pp. 322-323.
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- Gas Dissociation, The Theory of.** By OTTO STEEN. *Annealen der Physik*, Series 4, Vol. 44, 1914, No. 12, pp. 497-524.
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- Heat Economy in the Tar and Petroleum Industry.** By P. W. UHL-MANN. *Chemische Apparatur*, Vol. 1, 1914, No. 12, pp. 177-179.
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- Zinc, Physico-Chemical Studies on.** By ERNST COHEN AND W. D. HELDERMAN. *Zeitschrift fuer physikalische Chemie*, Vol. 87, 1914, No. 4, pp. 426-430.
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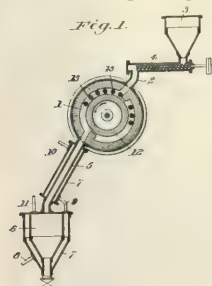


# RECENT INVENTIONS

By C. L. PARKER, Solicitor of Chemical Patents, McGill Building, Washington, D. C.

## Manufacturing Nitrogen

**Compounds.** T. Fujiyama, March 17, 1914. U. S. Pat. 1,090,391. This apparatus is designed for producing nitrogen compounds from carbids by the action of nitrogen. In the chamber 1 is mounted roller 12 made of fire-proof material. Carbon rods 13 capable of producing electric arcs or carbon resistors are arranged in an annular series for heating the chamber. The material is brought on to roller 12 from pipe 2 and is said to absorb nitrogen while moving to the discharge pipe 5 which is water-jacketed to prevent decomposition of the nitrogen compounds produced.



pounds produced.

**Synthetic Caoutchouc.** C. K. F. L. Gross, March 24, 1914. U. S. Pat. 1,090,847. Isoprene is heated in contact with trioxymethylene until a viscous mass is obtained.

**Potash from Feldspar.** H. P. Bassett, March 24, 1914. U. S. Pat. 1,091,034. Feldspar is mixed with sodium acid sulfate, sodium chlorid, and a reducing agent, the reducing agent being employed in such quantity as to reduce only a part of the sulfate to sulfid. The mixture is heated to a bright red heat for from one to two hours and the water-soluble portion of the remaining mass is separated and the potash recovered from it.

**Treating Metals.** E. G. Gilson, March 24, 1914. U. S. Pat. 1,091,057. Metals are heated in a non-oxidizing atmosphere in contact with aluminum, aluminum oxid and a chlorid in order to render them inoxidizable.

**Extracting Potassium and Sodium Compounds from Silicates which Contain Alkalis.** A. Messerschmitt, March 24, 1914. U. S. Pat. 1,091,230. Soluble sodium and potassium compounds are produced from feldspar and similar materials by finely dividing such material and mixing it with a slime containing undried precipitated calcium carbonate resulting from a soda manufacturing process. The mixture is heated to a decomposing temperature and lixiviated.

**Sulfur Dioxid.** H. K. Moore and R. B. Wolf, March 31, 1914. U. S. Pat. 1,091,689. Sulfur-bearing materials are burned and the products of combustion passed through a circulating body of refrigerated solvent for the sulfur dioxid gas such as an aqueous calcium chlorid solution maintained at a temperature of approximately 32° F. The sulfur dioxid gas is extracted *in vacuo* from the solvent and refrigerated *in vacuo* to liquefy it.

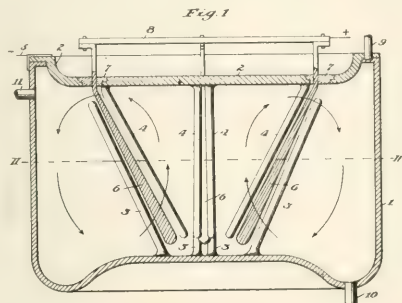
**Ammonia Production.** S. Peacock, April 7, 1914. U. S. Pat. 1,092,167. Ammonia is produced from a higher iron hydrid in the presence of free nitrogen by causing the iron hydrid to split off a portion of its hydrogen at a temperature suitable for the nascent hydrogen thus produced to combine with the free nitrogen to form ammonia. Free hydrogen is simultaneously fed to the mass to reform the higher iron hydrid as fast as the ammonia is produced.

**Making Catalysts.** C. Ellis, April 7, 1914. U. S. Pat. 1,092,206. An arc is formed between nickel electrodes in the presence of water and the finely divided nickel containing precipitate resulting from the eroding action of the arc is collected.

**Process of Making Chlorates.** G. Kolsky, April 7, 1914. U. S. Pat. 1,092,369. Chlorates are produced by passing an

electric current through a suitable electrolyte between electrode surfaces separated only by the electrolyte. Such evolution of gas at the electrodes is maintained as will suffice to induce an active circulation of the electrolyte past the electrodes and effect depolarization, the lines of flow of the electrolyte passing electrodes of opposite polarity in rapid succession.

In the use of the apparatus illustrated for the manufacture of

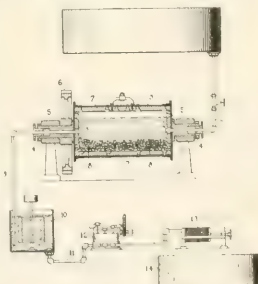


potassium chlorate, a considerable body of liquid is subjected to electrolytic action for several hours or until the percentage of chlorate has risen to a desired degree, whereupon the liquid is withdrawn and replaced by fresh electrolyte. There is no continuous flow of electrolyte into and from the apparatus, the circulation of liquid being due solely to the evolution of hydrogen at the electrodes.

**Composition for Use in Matches.** H. Staier, April 7, 1914. U. S. Pat. 1,092,408. A substitute for yellow phosphorus in the manufacture of match compositions is produced by thoroughly mixing red phosphorus, a metallic sulfid and sulfur in the proportions by weight of six parts of red phosphorus, two parts of metallic sulfid and three parts of sulfur. The mixture is heated to a temperature of about 500° F., washed with water at a high temperature and dried.

**Precipitation of Metals from Cyanid Solutions.** C. Butters, April 7, 1914. U. S. Pat. 1,092,765. Precious metals have been

precipitated from cyanid solutions by the action of aluminum in the form of dust. To avoid the expense of reducing aluminum to dust form, the patentee employs aluminum in granular form, disposed within a rotating mill through which the cyanid solution is conducted. The attrition to which the granular pieces are continually subjected prevents the formation upon their surfaces of a deposit which would arrest the chemical action.



**Hardening or Treatment of Steel.** A. W. Machlet, April 14, 1914. U. S. Pat. 1,092,925. The iron or steel under treatment is heated to at least a red heat in an atmosphere of ammonia which has been passed or filtered through kerosene and then in an atmosphere of ammonia alone.

# MARKET REPORT

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR THE MONTH OF JULY, 1914

## ORGANIC CHEMICALS

Acetanilid.....	Lb.	21 1/4	@	22
Acetic Acid (28 per cent).....	C.	1.50	@	1.65
Acetone (drums).....	Lb.	10 1/2	@	11
Alcohol, denatured (180 proof).....	Gal.	33	@	35
Alcohol, grain (188 proof).....	Gal.	2 1/8	@	2.50
Alcohol, wood (95 per cent).....	Gal.	4.55	@	4.7
Amyl Acetate.....	Lb.	1.55	@	1.60
Aniline Oil.....	Lb.	10 1/2	@	10 1/4
Benzoic Acid.....	Lb.	23	@	27
Beuzol (90 per cent).....	Gal.	23	@	25
Camphor (refined in bulk).....	Lb.	44 1/2	@	44 1/2
Carbolic Acid (drums).....	Lb.	7 1/2	@	9
Carbon Bisulfide.....	Lb.	6 1/2	@	8
Carbon Tetrachloride (drums).....	Lb.	7 3/4	@	7 3/4
Chloroform.....	Lb.	19	@	24
Citric Acid (domestic), crystals.....	Lb.	3	@	5 1/4
Dextrine (corn).....	C.	2 1/2	@	3 0/2
Dextrine (imported potato).....	Lb.	4 1/4	@	5
Ether (U. S. P., 1900).....	Lb.	18	@	24
Formaldehyde.....	Lb.	8 1/2	@	9 1/2
Glycerine (dynamite).....	Lb.	19	@	19 1/2
Oxalic Acid.....	Lb.	7 1/4	@	7 1/2
Pyrogallol Acid (bulk).....	Lb.	1 20	@	1.40
Salicylic Acid.....	Lb.	2 1/2	@	2 5
Starch (cassava).....	Lb.	3 1/4	@	4
Starch (corn).....	C.	1 9/10	@	2.10
Starch (potato).....	Lb.	4	@	4 1/4
Starch (rice).....	Lb.	7	@	8
Starch (sago).....	Lb.	2 1/4	@	2 3/4
Starch (wheat).....	Lb.	4 1/4	@	5 1/4
Tannic Acid (commercial).....	Lb.	33	@	36
Tartaric Acid, crystals.....	Lb.	30 1/4	@	—

## INORGANIC CHEMICALS

Acetate of Lead (brown, broken).....	Lb.	7 1/4	@	7 1/2
Acetate of Lime (gray).....	C.	1.50	@	1.55
Alum (lump).....	C.	1.75	@	2.00
Aluminum Sulfate (high-grade).....	C.	1.25	@	1.75
Ammonium Carbonate, domestic.....	Lb.	8	@	8 1/2
Ammonium Chloride, gray.....	Lb.	5 1/2	@	6 1/8
Aqua Ammonia (drums) 16°.....	Lb.	2 1/4	@	2 1/2
Arsenic, white.....	Lb.	3	@	3 1/4
Barium Chloride.....	Lb.	1 1/4	@	1 1/4
Barium Nitrate.....	Lb.	5	to	5 1/4
Barytes (prime white, foreign).....	Ton	19.00	@	23.50
Bleaching Powder (35 per cent).....	C.	1.20	@	1.25
Blue Vitriol.....	C.	4.50	@	4.70
Borax, crystals (bags).....	Lb.	35 1/4	@	41 1/2
Boric Acid, crystals (powd.).....	Lb.	7 1/8	@	8
Brimstone (crude, domestic).....	Ton	22.00	@	22.50
Bromine, bulk.....	Lb.	30	@	35
Calcium Chloride, fused.....	C.	60	@	65
Chalk (light precipitated).....	Lb.	4	@	4 1/2
China Clay (imported).....	Ton	14.00	@	16.00
Feldspar.....	Ton	8.00	@	12.00
Fuller's Earth, powdered, Foreign.....	Ton	16.00	@	17.00
Green Vitriol (bulk).....	C.	55	@	60
Hydrochloric Acid (18°).....	C.	1.15	@	1.65
Iodine (resublimed).....	Lb.	3.55	@	3.60
Lead Nitrate.....	Lb.	8 1/8	@	8 1/2
Litharge (American).....	Lb.	5 1/2	@	5 1/4
Lithium Carbonate.....	Lb.	65	@	70
Magnesium Carbonate.....	Lb.	21	@	35
Magnesite "Calced".....	Ton	28.50	@	29.50
Nitric Acid, 36°.....	Lb.	37 1/8	@	41 1/4
Phosphoric Acid (sp. gr. 1.75).....	Lb.	20	@	24
Phosphorus.....	Lb.	45	@	1.00
Plaster of Paris.....	Bbl.	1.50	@	1.70
Potassium Bichromate, 50°.....	Lb.	6 1/4	@	7
Potassium Bromide.....	Lb.	39	@	40
Potassium Carbonate (calced), 80 @ 85%.....	C.	3	@	3 1/4
Potassium Chlorate, crystals.....	Lb.	7 1/4	@	7 3/4
Potassium Cyanide (bulk), 98-99%.....	Lb.	19	@	22
Potassium Hydroxide.....	C.	4.35	@	5.00
Potassium Iodide (bulk).....	Lb.	2.95	@	3.00
Potassium Nitrate (crude).....	Lb.	4 1/4	@	5 1/4
Potassium Permanganate (bulk).....	Lb.	9 1/4	@	10
Quicksilver, Flask (75 lbs.).....	Lb.	35.50	@	36.00
Red Lead (American).....	Lb.	6	@	6 1/4
Salt Cake (glass makers').....	C.	55	@	65

Silver Nitrate.....	Oz.	34 1/4	@	36 1/2
Soapstone in bags.....	Ton	10.00	@	12.00
Soda Ash (48 per cent).....	C.	67 1/2	@	72 1/2
Sodium Acetate.....	Lb.	3 1/4	@	4 1/4
Sodium Bicarbonate (domestic).....	C.	1.00	@	1.10
Sodium Bicarbonate (English).....	Lb.	2 1/4	@	3
Sodium Bichromate.....	Lb.	4 1/4	@	5
Sodium Carbonate (dry).....	C.	60	@	80
Sodium Chlorate.....	Lb.	7 1/4	@	7 1/2
Sodium Hydroxide, 60 per cent.....	C.	1.55	@	1.57 1/2
Sodium Hyposulfite.....	C.	1.30	@	1.60
Sodium Nitrate, 95 per cent, spot.....	C.	2.07 1/2	@	2.10
Sodium Silicate (liquid).....	C.	65	@	1.50
Strontium Nitrate.....	Lb.	6 1/4	@	7
Sulfur, Flowers (sublimed).....	C.	2.20	@	2.60
Sulfur, Roll.....	C.	1.85	@	2.15
Sulfuric Acid, 60° B.....	C.	85	@	1.00
Talc (American).....	Ton	15.00	@	20.00
Terra Alba (American), No. 1.....	C.	75	@	80
Tin Bichloride (50°).....	Lb.	11 1/4	@	12 1/2
Tin Oxide.....	Lb.	35	@	37
White Lead (American, dry).....	Lb.	5 1/4	@	5 1/2
Zinc Carbonate.....	Lb.	8 1/2	@	9
Zinc Chloride (granulated).....	Lb.	4 1/2	@	5
Zinc Oxide (American process).....	Lb.	5 1/4	@	6 1/4
Zinc Sulfate.....	C.	2.35	@	2.70

## OILS, WAXES, ETC.

Beeswax (pure white).....	Lb.	47 1/2	@	50
Black Mineral Oil, 29 gravity.....	Gal.	13 1/4	@	14
Castor Oil (No. 3).....	Lb.	8	@	8 1/4
Ceresin (yellow).....	Lb.	12	@	22
Corn Oil.....	C.	6.35	@	6.40
Cottonseed Oil (crude), f. o. b. mill.....	Gal.	47	@	—
Cottonseed Oil (p. s. y.).....	Lb.	7 1/4	@	—
Cylinder Oil (light, filtered).....	Lb.	21 1/2	@	32
Japan Wax.....	Lb.	11	@	11 1/2
Lard Oil (prime winter).....	Gal.	92	@	95
Linseed Oil (raw).....	Gal.	53	@	54
Menhaden Oil (crude).....	Gal.	32 1/2	@	35
Neatsfoot Oil (20°).....	Gal.	96	@	98
Paraffine (crude, 120 & 122 m. p.).....	Lb.	3 1/4	@	3 1/4
Paraffine Oil (high viscosity).....	Gal.	27	@	28
Rosin ("F" grade) (280 lbs.).....	Bbl.	4.30	@	—
Rosin Oil (first run).....	Gal.	—	@	27
Shellac, T. N.....	Lb.	14 1/2	@	15
Spermaceti (cake).....	Lb.	30	@	31
Sperm Oil (bleached winter), 38°.....	Gal.	70	@	71
Spindle Oil, No. 200.....	Gal.	18	@	19
Stearic Acid (double-pressed).....	Lb.	8 1/4	@	9
Tallow (acidless).....	Gal.	64	@	66
Tar Oil (distilled).....	Gal.	30	@	31
Turpentine (spirits of).....	Gal.	48 1/2	@	50

## METALS

Aluminum (No. 1 ingots).....	Lb.	17 1/2	@	18
Antimony (Hallet's).....	Lb.	6 1/4	@	7 1/4
Bismuth (New York).....	Lb.	2.05	@	2.10
Bronze powder.....	Lb.	50	@	3.00
Copper (electrolytic).....	C.	13.52 1/2	@	—
Copper (lake).....	C.	13.67 1/2	@	—
Lead, N. Y.....	C.	3.90	@	—
Nickel.....	Lb.	50	@	55
Platinum (refined).....	Oz.	43.50	@	44.50
Silver.....	Oz.	54 1/2	@	—
Tin.....	C.	32 10	@	33 00
Zinc.....	C.	5.00	@	5 10

## FERTILIZER MATERIALS

Ammonium Sulfate.....	C.	2.55	@	2.57 1/2
Blood, dried.....	Unit	3.25	@	—
Bone, 4 1/2 and 50, ground, raw.....	Ton	30.00	@	—
Calcium Cyanamide.....	Unit of Ammonia	2.17 1/2	@	2.20
Calcium Nitrate (Norwegian).....	C.	2.05	@	2.15
Castor meal.....	Unit	3.25	@	—
Fish Scrap, domestic, dried.....	Unit	2.90	@	—
Phosphate, acid, 16 per cent bulk.....	Ton	7.00	@	10
Phosphate rock; f. o. b. mine.....	Ton	2.25	@	2.50
Florida land pebble, 68 per cent.....	Ton	5.00	@	5.50
Tennessee, 70-80 per cent.....	Ton	39.07	@	—
Potassium, "muriate," basis 80 per cent.....	Ton	—	@	—
Pyrites, furnace size, imported.....	Unit	0.13 1/4	@	—
Tankage, high-grade.....	Unit	3.10	@	3.20 & 10

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## TABLE OF CONTENTS

MONTREAL MEETING POSTPONED .....	706	CURRENT INDUSTRIAL NEWS:	
ORIGINAL PAPERS:		Ammonium Chloride, a New By-product of Gas Works, etc.....	778
Synthetic Celite and Large Crystals of Tricalcic Silicate. By Edward D. Campbell.....	706	Stockholm Gas-Works in 1913.....	779
Hypothetical Combinations in Water Analysis. By R. B. Dole .....	710	Carbon Monoxide and Nitric Oxide from Heating and Lighting Burners.....	779
Chemistry of the Bleaching of Cotton Cloth. By John C. Hebdlen.....	714	Oil in Australia.....	779
The Chemistry of Pine Oil. By Maximilian Toch.....	720	Canadian Coal.....	779
Oils of the Coniferae. I—The Leaf and Twig Oils of Cuban and Longleaf Pines and the Cone Oil of Longleaf Pine. By A. W. Schorger.....	723	British Coal Exports in the First Half of 1914.....	779
The Specific Heat of California Petroleum. By Harold E. Wales.....	727	The Altiore Process of Die-Casting.....	779
Determination of Silver and Base Metal in Precious Metal Bullion. By Frederic P. Dewey.....	728	A New Bearing Metal.....	780
The Effect of Bread Wrapping on the Chemical Composition of the Loaf. By H. E. Barnard and H. E. Bishop.....	736	English Trade Unions in 1912.....	780
Some Data on Peanut Butter. By C. A. A. Utt.....	746	Automatic Equipment for Placing Powders in Bottles on Net Weight Basis.....	780
The Influence of Sulfur on Soil Acidity. By H. Clay Lint.....	747	Decreased Activity in English Shipbuilding.....	781
The Ferric Alum Estimation of Caseine. By H. V. Army and H. H. Schaefer.....	748	American Railroads.....	781
Studies in Synthetic Drug Analysis: II—Estimation of Antipyrin. By W. O. Emery and S. Palkin.....	751	Steam Power Used for Generation of Electric Current in Prussia.....	781
The Determination of Mercuric Iodide in Tablets. By A. W. Bender.....	753	Diesel Engines in the Italian Navy.....	781
LABORATORY AND PLANT:		Calcium Carbide, Cyanamide and Nitrate.....	781
The Development of the Rotary Kiln and Its Application to Various Chemical and Metallurgical Processes. By Richard K. Meade.....	754	Mineral-Water Production in 1912.....	781
A Combination Water Softener and Storage Tank. By L. M. Booth.....	760	NOTES AND CORRESPONDENCE:	
A New Seal for the Prevention of Aeration in Deaerated Liquids. By Frank Bachmann.....	764	Obituary—Russell S. Penniman.....	782
ADDRESSES:		The Stability of Resin Acids at Slightly Elevated Temperatures—A Correction.....	782
Shoddy and Carbonized Waste. By Louis Joseph Mátos.....	765	Exhibition Mine at the Panama-Pacific Exposition.....	782
Chemical Engineering. By Charles S. Palmer.....	768	Industrial Accidents in Pennsylvania in 1912.....	783
CHANDLER FOUNDATION LECTURE:		PERSONAL NOTES.....	783
Some Aspects of Industrial Chemistry. By L. H. Baekeland.....	769	GOVERNMENT PUBLICATIONS.....	784
		BOOK REVIEWS: A Textbook of Thermodynamics; Industrial Organic Analysis; Die Industrie der Cyanverbindungen, ihre Entwicklung und ihre gegenwaertiger Stand (The Industry of the Cyanogen Compounds, Its Development and Its Present Condition); The Chemistry of Cattle Feeding and Dairying.....	787
		NEW PUBLICATIONS.....	789
		RECENT INVENTIONS.....	790
		MARKET REPORT.....	792



## MONTREAL MEETING POSTPONED

The postponement of the Montreal Meeting, just announced by the officers of the Society, will be a great disappointment to the many chemists who have been looking forward to this event with keen anticipation and pleasure. Many have scarcely realized the far-reaching effects of the war in Europe, while the seriousness of the situation is pressing heavily and in an ever-increasing variety of forms upon other members of our profession.

Conditions in Canada which necessitated the postponement may be best conveyed by the following letter to Secretary Parsons from Prof. R. F. Ruttan, Chairman of the Montreal Committee:

DEAR DR. PARSONS:

The declaration of war between Germany and England found me at Metis Beach, 500 miles down the St. Lawrence, playing golf with a feeling of relief that our organization for the meeting was so complete.

We had a meeting of all the Executive Committee in town this afternoon, and with profound regret, fully realizing what it meant to you and the Society, decided that the meeting could not be made a success in British territory this autumn. I wired you at once as follows:

"Canada is sending the first contingent of 20,000 very soon and a second and third will follow.

"Montrealers feel that we are at war with Germany and Austria, and are behaving as if the enemy were threatening us.

"The Harbor, canals, etc., are under Martial Law. The excursions were off, as the company canceled our contract for the steamers for the rapids and harbor.

"No German member of the Society would naturally come to British soil and all with German names would be questioned at the boundary. Many are even now turned back. We felt that the exclusion of so many prominent members of the Society was a high price to pay for a meeting here.

"Any foreigners would be subjected to disagreeable formalities and conditions on coming here just now.

"It would be impossible to attract to the Convention the slightest public interest in Montreal, outside a few dozen chemists. No one would come to the *Conversazione* or the garden parties we had arranged, and while there would surely be the feeling of good fellowship among ourselves, it would be overshadowed by the tragic war we are in at present."

It is sad to look over the wreck of our hopes of a big and successful meeting. Everything was organized and under way

even to rehearsing for the Smoker. The toastmaster and speakers for the banquet, the chemical and other scientific "stunts" for the *Conversazione* were arranged and the hall for the exhibits prepared, which, by the way, would have been of exceptional interest. We feel very sad about it all today I assure you.

The Principal and Vice-Principal (of McGill University) and Sir Wm. Osler, who had promised to speak at the banquet, are in Europe, as well as many of our staff. Their return is uncertain. Everything was against the meeting and only our desire to give you the hand of good fellowship and the advanced state of the preparations made us hesitate at all about calling everything off.

I hope you appreciate our situation and that we have your sympathy.

I came up this morning feeling sure the meeting would go, but have been convinced it could not be made more than an apology for a convention, which it would be a waste of time to attend.

When things settle down again we shall once more extend you an invitation, and hope you will do us the honor of accepting it.

I am, with kindest regards,

Sincerely yours,

(Signed) R. F. RUTTAN

The officers of the Society acted promptly upon the advice of the committee and issued notice of indefinite postponement of the Annual Meeting of 1914.

It now seems improbable that any meeting of the Society will be held this fall.

The question of transferring the convention to another place was considered but in view of the tremendous influence of events now pending and the important duties which will devolve upon the chemical profession, alike in neutral and in involved countries, it was the almost unanimous opinion of the officers of the Society that it will be impossible to arrange for a successful meeting early in the fall and that business conditions throughout the country render it improbable that it would be advisable to have a meeting later in the year. This latter point, however, will be definitely decided later and any notice that may become necessary will appear in the October or November journals.

We believe the decision of the officers will be unanimously approved by the membership of the Society.

## ORIGINAL PAPERS

### SYNTHETIC CELITE AND LARGE CRYSTALS OF TRICALCIC SILICATE

By EDWARD D. CAMPBELL

Received June 26, 1914

"Törnebohm and Le Chatelier as early as 1897 described 'alite' as the crystalline material separating out from an inter-crystalline magma 'celite.' Törnebohm<sup>1</sup> further lays stress on the fact that celite is fusible at the ordinary clinkering temperature and promotes the crystallization of the alite. No claim

is made that alite is a definite chemical or mineralogical entity and it is according to this interpretation of the terms that they are used in this article."

In the work done last year<sup>1</sup> discs of well burned clinker, made from the raw material from one of the leading cement mills in the Lehigh Valley, were placed between discs of pure magnesium oxide, MgO, and the pile so constructed heated to various temperatures ranging from 1475° to 1575° C. The portion of the clinker constituting the celite as defined by

<sup>1</sup> *Technische Z.*, 21 (1897), 1148

<sup>1</sup> This Journal, 5, 627.

Törnebohm and Le Chatelier and amounting to from twenty (20) to twenty-seven (27) per cent of the weight of the clinker was liquefied and absorbed by the magnesium oxide, MgO, discs. From analyses of the discs saturated with celite the percentage composition of this latter and its molecular ratios could be calculated. The results are given in the following table:

Experiment	Temperature °C.	Time Hrs.	Per cent celite	Percentage composition					
				SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	
A <sub>1</sub> .....	1475	13	20.87	11.21	19.28	8.30	55.89	5.32	
A <sub>2</sub> .....	1510	3	21.40	13.63	18.24	7.99	55.20	4.95	
A <sub>3</sub> .....	1575	2 1/2	26.25	13.64	18.11	7.94	55.36	4.96	
B <sub>1</sub> .....	1575	8	20.80	14.46	17.36	8.12	55.91	4.15	
				14.39	17.34	8.22	55.91	4.15	
				9.13	19.89	8.87	59.18	2.92	
				9.07	19.86	8.99	59.15	2.93	

The molecular ratios of the celite calculated from the means of the analyses in Table I and reduced to the basis of one hundred (100) molecules of R<sub>2</sub>O<sub>3</sub> (Al<sub>2</sub>O<sub>3</sub> + Fe<sub>2</sub>O<sub>3</sub>) are given in Table II.

TABLE II - RATIOS IN CELITE ABSORBED  
100 R<sub>2</sub>O<sub>3</sub>

Experiment	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	CaO	MgO	RO
A <sub>1</sub> .....	78.4	21.6	77.1	413	54.65	467.65
A <sub>2</sub> .....	78.1	21.9	99.3	433.5	53.9	487.4
A <sub>3</sub> .....	76.9	23.1	108.2	451.5	46.5	498.0
B <sub>1</sub> .....	77.7	22.3	58.9	426.5	29.0	455.5

It has seemed better to calculate the molecular ratios given in Table II to a basis of 100 molecules of R<sub>2</sub>O<sub>3</sub> (Al<sub>2</sub>O<sub>3</sub> + Fe<sub>2</sub>O<sub>3</sub>) instead of to a basis of 100 molecules of Al<sub>2</sub>O<sub>3</sub> alone, on account of some of the conclusions which were drawn last year and which were as follows: (1) "That although the proportion of ferric oxide, Fe<sub>2</sub>O<sub>3</sub>, to the alumina, Al<sub>2</sub>O<sub>3</sub>, is a little higher in the celite than in the alite, the difference is not very marked and the assumption that the ferric oxide is molecularly equivalent to alumina so far as the formation of celite goes seems justifiable although the hydraulic properties of the aluminates and ferrites differ in degree." (2) "With a given basicity of the mass as a whole the proportion of silica to alumina and ferric oxide in the celite increases with the temperature." (3) "With a given temperature, the proportion of silica to the alumina and ferric oxide in the celite decreases as the basicity of the mass as a whole increases."

The hypothesis was also advanced at that time, "That alite consists essentially of a calcium aluminate fusible at a little above 1400° and capable of dissolving, when liquid, calcium orthosilicate and calcium oxide, this latter being the more readily soluble, and that the solubilities of the orthosilicate and calcium oxide follow laws parallel to those which govern the solubilities of salts in liquid solution. No evidence is yet forthcoming to enable the chemical constitution of the pure fusible aluminate to be given so that no chemical formula is suggested for it."

The experimental work described in the present paper was carried on under the author's direction by R. A. Price and H. Y. Tang. The object of this work was to obtain perfectly fluid materials of the same molecular ratios as the celites obtained last year and thus obtain experimental evidence which should test the correctness of the proposed hypothesis.<sup>1</sup>

In order to reduce the problem to its simplest terms it was thought best to select materials as free as practicable from ferric oxide, Fe<sub>2</sub>O<sub>3</sub>, and magnesium oxide, MgO. The materials decided upon were a carefully washed kaolin, pure aluminum oxide, Al<sub>2</sub>O<sub>3</sub>, finely ground and washed quartz sand and chemically pure calcium carbonate. These materials thoroughly dried and analyzed were accurately weighed and mixed in the proportions of kaolin 400 grams, Al<sub>2</sub>O<sub>3</sub> (pure) 470 grams, C. P. CaCO<sub>3</sub> 2151 grams. The weighed materials were placed in a porcelain jar mill and revolved for three hours in order to insure uniform mixture. This base mixture was calculated to give on fusion a material of the following percentage composition: SiO<sub>2</sub> 9.17, Al<sub>2</sub>O<sub>3</sub> 30.91, Fe<sub>2</sub>O<sub>3</sub> 0.23, CaO 59.61, undetermined 0.07 and molecular ratio, calculated to the basis of 100 molecules of R<sub>2</sub>O<sub>3</sub>(Al<sub>2</sub>O<sub>3</sub> + Fe<sub>2</sub>O<sub>3</sub>): Al<sub>2</sub>O<sub>3</sub> 99.54, Fe<sub>2</sub>O<sub>3</sub> 0.46, SiO<sub>2</sub> 50, CaO 350, which reduced to its lowest terms would give an empirical formula of 2R<sub>2</sub>O<sub>3</sub>.SiO<sub>2</sub>.7CaO. By using this "C" mixture and adding pure silica, SiO<sub>2</sub>, and calcium carbonate, CaCO<sub>3</sub>, the ratio of silica and calcium oxide to alumina could be easily made the same as that found to exist in any of the celites recovered from cement clinker.<sup>1</sup>

It was found by experience that it was necessary to use a large platinum crucible in order to retain the fluid celite. The crucible used was a flat-bottomed cylindrical one 47 X 50 mm. and capable of holding about 100 grams of the raw mixture so that the weight of material after fusion was in the neighborhood of 60 grams.

The fusions were effected in a furnace substantially the same as the one described in our previous article, the temperatures being controlled and measured by the same methods that were employed in our former experiments. If an oxidizing atmosphere is maintained in the furnace the deterioration of the thermal couple is not great, amounting in the present case to only one (1) per cent after two years' use. The accompanying temperature readings have been corrected for this change. The dense vitreous mass found in the bottom of the crucible after each fusion could be removed only by shattering with a steel chisel and tapping the outside to loosen the pieces from the platinum.

Fusions were made of the "C" mixture alone and also of a mixture made by adding, in accurately weighed amounts, pure silica, SiO<sub>2</sub>, and pure calcium carbonate, CaCO<sub>3</sub>, to the "C" mixture in such proportions that the molecular ratios were the same as those found by analysis of the A<sub>3</sub> celite (Table II), the only difference being that in the C<sub>1</sub> celite the R<sub>2</sub>O<sub>3</sub> was practically all Al<sub>2</sub>O<sub>3</sub> and the RO all CaO. This would give for the C<sub>1</sub> celite the following percentage composition: SiO<sub>2</sub> 13.74, Al<sub>2</sub>O<sub>3</sub> 23.35, Fe<sub>2</sub>O<sub>3</sub> 0.17, CaO 62.74. The molecular ratio would then be 99.54 Al<sub>2</sub>O<sub>3</sub>, 0.46 Fe<sub>2</sub>O<sub>3</sub>, 99.3 SiO<sub>2</sub>, 487.4 CaO.

In preparing the C<sub>1</sub> fusions the raw mixture was placed in the platinum crucible and the furnace heated over night by an ordinary Meker, the temperature

<sup>1</sup> THIS JOURNAL, 5, 627.

<sup>1</sup> THIS JOURNAL, 5, 627.

reaching over  $1150^{\circ}$  by morning, when the Méker blast was put on and the temperature raised to well above the fusion point,  $1585^{\circ}$ – $1590^{\circ}$ , at which temperature it was held for from 2–3 hours; when it was judged that the solution was complete the temperature was gradually lowered, from 4–6 hours being required to bring the temperature down to about  $1415^{\circ}$ , after which the burner was turned out and the openings in the furnace closed and the whole allowed to cool over night.

The fusions of the C mixture alone were not cooled by gradually lowering the temperature but merely by closing up the furnace and letting it cool. That this method of slow cooling between the highest temperature of fusion and  $1415^{\circ}$  produced well defined crystals is shown by the slightly magnified photograph of a section of one of the pieces of  $C_1C$  celite in Plate I.

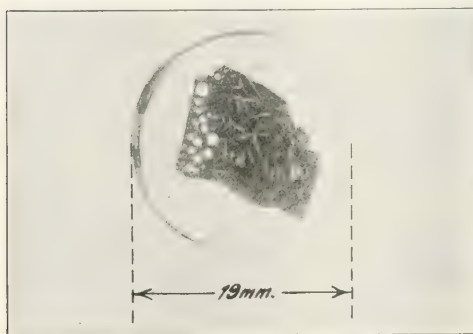


PLATE I

The crystals of the  $C_1d$  celite which was the most slowly cooled from the maximum temperature were even larger than those of  $C_1C$  celite.

To study the hydraulic properties some of the  $C_b$  celite and  $C_1C$  celite was ground to pass through a 200 mesh sieve. On mixing with water the material takes a flash initial set and takes its final set under a Gilmore needle in from 10–12 minutes. If after adding water enough for normal consistency the material is worked for 4 or 5 minutes under the spatula it becomes slower setting, about 10 minutes being required for the initial set and 24 hours or more for the final.

Pats of the  $C_1C$  and  $C_b$  celites made by working under the spatula until the flash set was past were placed in cold water, after 24 hours' standing in moist air and submitted to the usual 24 hour boiling test. In both cases the pats gave a perfect boiling test, there being no signs of warping or cracking, although they were not quite as strong or hard as a good Portland cement.

#### TRICALCIC SILICATE CRYSTALS

As the sections of  $C_1C$  and  $C_1d$  celites showed them to contain large well-developed crystals imbedded in the solvent in which they had formed the next step was to remove this latter in order to recover the crystals in as pure a condition as possible. To effect the removal of the fusible solvent from the crystals the same

principle was used as that employed in the removal of celite as described in a former paper.<sup>1</sup> Four weighed discs of pure magnesium oxide,  $MgO$ , were placed in the furnace and the temperature raised over night to a little over  $1100^{\circ}C$ . Three weighed pieces of the  $C_1d$  celite were placed in a pure magnesium oxide,  $MgO$ , dish made by cutting down a crucible.

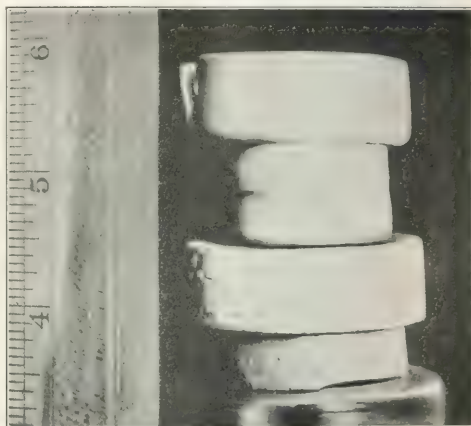


PLATE II

The dish containing the pieces was placed in the hot furnace and the blast put on in order to raise the temperature above the melting point of the solvent in as short a time as possible. Forty-five minutes after the dish was put in the furnace the temperature read  $1470^{\circ}C$ . and it was held within five degrees of  $1465^{\circ}C$ . for three hours and then raised at the rate of  $25^{\circ}C$ . per hour during a period of five hours, reaching  $1590^{\circ}$ .



PLATE III

$C$ . eight hours after the melting point of the solvent had been passed. The furnace was then closed and allowed to cool over night. On removing the dish and discs they were found to be firmly cemented together by the absorbed celite while the residue in

<sup>1</sup> THIS JOURNAL, 5, 627.



the dish consisted of a mass of thin plate-like, interlocking crystals from which the solvent had been almost completely drained away.

The three pieces of celite placed in the dish weighed 18.312 grams and the residue weighed 6.123 grams; thus 66.56 per cent was absorbed and 33.44 per cent recovered as crystals. The crystals were broken apart and some of the best ones selected for chemical analysis and determination of their optical properties.

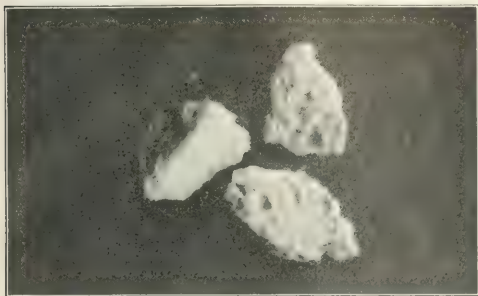


PLATE IV

The appearance of the materials after the absorption is given in the accompanying photographs. Plate II is a side view showing the four magnesium oxide, MgO, discs with the magnesium oxide, MgO, dish at the top. Plate III is a top view of the dish showing the three masses of crystals in place. Plate IV shows the masses of crystals inverted to show better the crys-

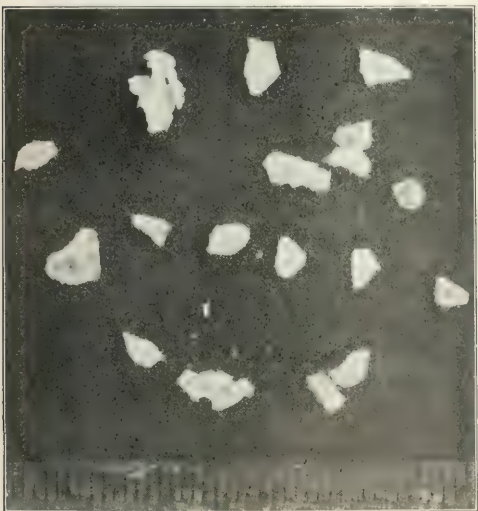


PLATE V

tal faces and Plate V shows some of the individual crystals together with a centimeter scale graduated in millimeters. It will be noticed in this photograph that some of these crystals were nearly seven millimeters in length.

Analyses of selected crystals gave the following results:

	SiO <sub>2</sub> Per cent	Al <sub>2</sub> O <sub>3</sub> Per cent	CaO Per cent
I.....	73.74	5.47	70.71
II.....	23.50	.....	70.78

Using the first analysis the molecular ratio calculated to the basis of one hundred molecules is 100 SiO<sub>2</sub>, 13.6 Al<sub>2</sub>O<sub>3</sub>, 320.3 CaO. If we deduct from the total CaO enough to form tricalcic silicate the 20.3 molecules left to combine with the 13.6 Al<sub>2</sub>O<sub>3</sub> is within the limits of experimental error which would be required for a calcium aluminate of the formula 5CaO.3Al<sub>2</sub>O<sub>3</sub>. The specific gravity of a selected fragment of crystals determined by means of Thoulet's solution gave 3.002.

The mass of crystals showed a light green color, due probably to a thin film of adhering solvent since many individual crystals were almost perfectly colorless. The crystals are pseudo-hexagonal and show no cleavage. The average refractive index is 1.708 and the birefringence is very weak. The crystals are optically negative and appear biaxial. The optical axial angle 2E is exceeding small.

These results agree very closely with those reported by F. E. Wright<sup>1</sup> for the tricalcic silicate prepared by Shepherd and Rankin. His report reads as follows:

"3CaO.SiO<sub>2</sub>(CaO 73.59, SiO<sub>2</sub> 26.41)—This compound, which is not stable at its melting point, but changes into a mixture of free lime and orthosilicate at higher temperatures, crystallizes in small equant grains, colorless and apparently without cleavage. The average refractive index is approximately 1.715, and the birefringence is very weak, not over 0.005. Interference figures are difficult to obtain because of the weak birefringence and the fineness of the grains, which rarely measure over 0.03 mm. diameter. The grains appear uniaxial or biaxial with small optic axial angle and are optically negative. On some of the preparations cut nearly normal to the optic axis, especially on those from preparations containing a little Al<sub>2</sub>O<sub>3</sub>, fine twinning lamellae were observed with low extinction angles indicating possibly that the crystal system is monoclinic. The distinguishing optical features of this compound are equant development, lack of cleavage, weak birefringence, optically negative character with 2E small or zero, and refractive index about 1.715. It is an interesting fact that in preparing this compound from the mixed oxides at 1400° or 1500°, the compounds, free lime and orthosilicate, are first formed and these in turn unite to form the tricalcic silicate on longer heating."

These results still further confirm the existence of tricalcic silicate first stated to be the essential constituent of alite by Le Chatelier. The existence of this compound which had been questioned for some time received confirmatory evidence by the work of A. H. White<sup>2</sup> and still greater confirmation by that of Shepherd, Rankin and Wright above quoted.

The two upper pure magnesium oxide discs which were saturated with celite were ground up and the SiO<sub>2</sub>,

<sup>1</sup> THIS JOURNAL, 3, 211.

<sup>2</sup> *Ibid.*, 1, 5.

$\text{Al}_2\text{O}_3$  and  $\text{CaO}$  determined in four gram samples by substantially the same method of analysis as that employed in our previous work on the recovery of celite. The weights of the various constituents recovered were as follows:

Sample	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{CaO}$
A.....	0.0518	0.1377	0.0036	0.2704
B.....	0.0315	0.1369	0.0038	0.2694

The sum of these give the following percentage composition:

$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{CaO}$
11.17	29.67	0.79	58.37

Calculating from this analysis the molecular ratios on the basis of 100 molecules of  $\text{R}_2\text{O}_3$  ( $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ ) we have 98.3  $\text{Al}_2\text{O}_3$ , 1.7  $\text{Fe}_2\text{O}_3$ , 62.8  $\text{SiO}_2$ , 352.4  $\text{CaO}$ . If we subtract from the total  $\text{CaO}$  the amount theoretically necessary to form tricalcic silicate there would be left 164 molecules of  $\text{CaO}$  to combine with 100 molecules of  $\text{R}_2\text{O}_3$ . These figures indicate almost conclusively that the fusible aluminate constituting the solvent in celite is the one described by Shepherd, Rankin and Wright having the formula  $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$  and a melting point of about  $1390^\circ$ .

#### SUMMARY

The foregoing work confirms, in general, the hypothesis "That celite consists essentially of a calcium aluminate, fusible a little above  $1400^\circ$  and capable of dissolving, when liquid, calcium orthosilicate and calcium oxide," but we may now add that the aluminate has the formula  $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$  and that if the concentration of the calcium oxide,  $\text{CaO}$ , is sufficient and solution complete, pure tricalcic silicate will crystallize out on slow cooling. This also suggests a new theoretical formula for Portland cement.

The Le Chatelier formula first proposed was  $\text{X}(3\text{CaO} \cdot \text{SiO}_2) + \text{Y}(3\text{CaO} \cdot \text{Al}_2\text{O}_3)$ . This called for the calcium oxide  $\text{CaO}$ , by weight to equal  $2.8\text{SiO}_2 + 1.6\text{Al}_2\text{O}_3$ . This always gives in practice a large excess of free lime. The Newbery formula  $\text{X}(3\text{CaO} \cdot \text{SiO}_2) + \text{Y}(2\text{CaO} \cdot \text{Al}_2\text{O}_3)$  calls for calcium oxide by weight to equal  $2.8\text{SiO}_2 + 1.1\text{Al}_2\text{O}_3$  but still cannot be adhered to in practice without the cement carrying excess free lime. The formula which would be suggested by the work above described would be  $\text{X}(3\text{CaO} \cdot \text{SiO}_2) + \text{Y}(5\text{CaO} \cdot 3\text{Al}_2\text{O}_3)$  which would call for calcium oxide by weight to equal  $2.8\text{SiO}_2 + 0.9\text{Al}_2\text{O}_3$ . Such a formula would conform more closely with the results obtained in the best practice.

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## HYPOTHETICAL COMBINATIONS IN WATER ANALYSIS\*

By R. B. DOLE<sup>†</sup>

### INTRODUCTION

The procedures followed in determining the various mineral ingredients of natural waters have become fairly well standardized, the differences of opinion in

<sup>†</sup> *Am. J. Sci.*, [55] 29 (1909), 293.

\* Paper read before the Division of Water, Sewage, and Sanitation at the 49th Meeting of the American Chemical Society, Cincinnati, April, 6-10, 1914. Published by permission of the Director, United States Geological Survey.

<sup>†</sup> Chemist, United States Geological Survey.

that respect now being chiefly in regard to the accuracy with which determinations should be made. The form of reporting the result is, however, still a fruitful source of inconvenience and disagreement. The mineral constituents are variously reported in ionic form, in hypothetical combination, in oxide form, and in equivalent of calcium carbonate. This divergence of practice makes it impossible to compare the work of two chemists without definite knowledge of their methods of computation and laborious recalculation of their results. Consequently, an effort is being made to agree on a uniform manner of reporting results in connection with the formulation of standard methods for the analysis of water, now being conducted jointly by committees of the American Chemical Society, the American Public Health Association, and the Association of Official Agricultural Chemists. This paper discusses the present confusing condition and the advantages of reporting the actual facts of analysis in ionic form.

### FACT VERSUS OPINION

A statement of an analysis in hypothetical combinations is obviously a mixture of fact and opinion. The amounts of iron, calcium, sulfate, and other radicles are determined by various reactions; approximate separation of scaling from non-scaling constituents is effected by treatment with dilute alcohol; but further than this, ordinary chemical tests contribute little to knowledge regarding the chemical composition of mineral waters, and consequently the exact amounts of the different salts in solution are largely conjectural. Though salts are probably present it is a mathematical impossibility correctly to apportion the bases among the acids after having found only the amounts of the acids and bases present.

### COMMON FORMS OF COMBINATION

As this lack of definite information gives free rein to the imagination there are many opinions as to how the bases and acids should be combined. Though each method has ardent advocates, each is a personal selection whose excellence can be proved only by theory. In order to show the essential practical differences in schemes of combination and some of the confusion to which they lead, the most common methods have been applied to the analysis of the water of Missouri River shown in Table I. This chemical composition is not at all exceptional, but it has been

TABLE I ANALYSIS OF THE WATER OF MISSOURI RIVER NEAR RUEGG, MO.—RESULTS IN PARTS PER MILLION

CONSTITUENTS	Results of analysis	Reacting values
Silica ( $\text{SiO}_2$ )	29.0	
Iron ( $\text{Fe}$ )	0.5	0.0179
Calcium ( $\text{Ca}$ )	52.0	2.5948
Magnesium ( $\text{Mg}$ )	16.0	1.1336
Sodium ( $\text{Na}$ )	31.0	1.3454
Potassium ( $\text{K}$ )	6.5	0.1664
Carbonate radicle ( $\text{CO}_2$ )	0.0	0.0000
Bicarbonate radicle ( $\text{HCO}_2$ )	178.0	2.9192
Sulfate radicle ( $\text{SO}_4$ )	104.0	2.1632
Nitrate radicle ( $\text{NO}_3$ )	3.9	0.0467
Chlorine ( $\text{Cl}$ )	12.0	0.3384
Dissolved solids by evaporation	346.0	
Total reacting value of basic radicles		5.4381
Total reacting value of acid radicles		5.4675
Error of closure of reacting values		0.02 per cent

<sup>†</sup> U. S. Geol. Survey, *Water Supply Paper* 236, 80.

purposely selected because it represents a large group of waters in which carbonate is sufficient to satisfy

either calcium or magnesium but insufficient to satisfy both.

The first advantage of stating the actual facts of an analysis is seen by observing the reacting values or combining equivalents, which have been computed by multiplying the amount of each radicle by its valence and dividing the product by its molecular weight, for they indicate that the probable error of this analysis is about 0.3 per cent. When hypothetical combinations are made, one of three procedures is usually followed:

(1) All the bases and acids except the alkalis present in appreciable amount are estimated and the excess of acid is computed to an equivalent of sodium and potassium salts.

(2) All the bases and acids except carbonate are estimated and the excess of base computed to an equivalent of carbonates.

(3) All the bases and acids are determined and the figures representing the salts are "doctored" to balance. These practices effectually conceal errors of technique and leave it entirely to the judgment of the analyst whether his error of closure is reasonable, and the evidence on which his judgment is based is completely masked because his hypothetical combinations show no error at all. On the other hand, the probable accuracy of the work can be calculated directly from the ionic statement as indicated in the table.

Silica has not been included among either acids or bases. Some waters<sup>1</sup> of unusual character may contain the silicate radicle, but it is safe to conclude that it is absent from most natural waters. Whether silica is a colloid depends on our definition of colloid, but whatever it may be called it does not usually enter into the system of reactive bases and acids. This conclusion was reached several years ago by Kahlenberg and Lincoln,<sup>2</sup> and Kohlrausch<sup>3</sup> and others make practically the same statement. Among 8,000 analyses of surface waters from all parts of the United States the writer finds that if silicate is not included the acid radicles are in excess in 40 per cent and the basic radicles in 60 per cent of the analyses and that the difference either way amounts to only 1 or 2 parts per million, bears no mathematical relation to the quantity or the proportion of silica, and may as reasonably be explained by error of analysis as in any other way. This digression is inserted because it has been proposed to the committee to include rules for computing silica to silicates of the various bases.

Table II gives hypothetical combinations of the analytical data in Table I. All the sets of combinations represent schemes used either by a large number of analysts or by one or two concerns that examine many samples from all parts of the country. The list might be much more extensive. No extreme, but mathematically correct, schemes that are unused have been introduced, and the table has been further simplified by omitting all but the more commonly-measured constituents. The only difference between Columns 1 and 2 is that sodium nitrate is calculated in

one and potassium nitrate in the other. In Column 3, however, calcium is combined first with sulfate instead of carbonate. In Column 4, calcium is combined successively with sulfate, chlorine, and carbonate. Columns 6 and 7 represent methods used by certain boiler-water analysts, who ordinarily determine and

TABLE II—HYPOTHETICAL COMBINATIONS REPRESENTING ONE ANALYSIS (SEE TABLE I)

	1	2	3	4	5	6	7
SiO <sub>2</sub> .....	29	29	29	29	29	29	29
Fe <sub>2</sub> O <sub>3</sub> .....	1.6	1.6	1.6	0.7	1.6	0.7	0.7
Ca(HCO <sub>3</sub> ) <sub>2</sub> .....	210	210	36	8	126	130	210
CaSO <sub>4</sub> .....			147	147	68	68	
CaCl <sub>2</sub> .....			19	19			
Ca(NO <sub>3</sub> ) <sub>2</sub> .....					4		
Mg(HCO <sub>3</sub> ) <sub>2</sub> .....	20	20	96	96	96	96	24
MgSO <sub>4</sub> .....	62	62		1.8			60
NaHCO <sub>3</sub> .....	80	80	94		83	83	83
Na <sub>2</sub> SO <sub>4</sub> .....	10	13	10		10	20	20
NaCl.....	4		4				
NaNO <sub>3</sub> .....	12	9	12		1.2		
KCl.....		5					
KNO <sub>3</sub> .....							
Sum.....	429	430	430	428	430	427	427
Scale-forming constituents.....	233	233	255	257	236	235	236
Foaming constituents.....	106	107	80	82	105	103	103

report iron as the oxide and do not separate sodium and potassium but compute both together as sodium. As these analysts would not determine nitrate in a water containing so little as that under discussion absence of that radicle has necessarily been assumed. Bicarbonates instead of carbonates also have been computed because analysis shows that the carbonate radicle is absent; this slight deviation from the directed methods, however, makes no difference in the theory and permits direct comparison with other schemes. According to the scheme in Column 5 calcium nitrate, instead of potassium or sodium nitrate, is computed. According to that in Column 6 as much as possible of magnesium bicarbonate is computed first, while according to that in Column 7 as much as possible of calcium bicarbonate is computed first.

The most obvious deduction from these figures is that it is impossible to compare the report of one analyst with that of another without recalculation. The next thought that comes to most of us is that the other man's scheme is incorrect. Some would object to calculation of calcium nitrate at the expense of calcium carbonate and some to calculation of calcium chloride in the presence of sodium bicarbonate, while others would prefer to calculate magnesium sulfate instead of calcium sulfate. Aside from the theoretical merits of the methods, consideration of which would provoke endless discussion, there are these alarming facts:

(1) All are widely-used methods of reporting the analysis of one water.

(2) The results can not be directly compared with one another.

(3) The results are used for estimating the quality of the water.

(4) The results are given to men who, not being chemists, are incompetent properly to discount the statements but take them at their face value.

One more digression may be permitted for the purpose of referring to the sums of the computed constituents. The sums in the last half of the table are a little lower than the others because nitrate and ferrous carbonate are disregarded. If these con-

<sup>1</sup> Clarke, F. W., U. S. Geol. Survey, *Bull.* 491 (1911), 183.

<sup>2</sup> *Jour. Phys. Chem.*, 2 (1898), 77.

<sup>3</sup> *Z. Physik. Chem.*, 12 (1893), 773.



stituents had been computed all the sums would have been alike, the slight numerical differences among them being due to casting off decimals. Reference is made to this agreement because some chemists, no doubt thoughtlessly, consider their methods of combination correct because they "come out even." One reports that he never has any acid or base left over, or very little, and another that the sum of his calculated constituents agrees very closely with total solids by evaporation. These comments prove the excellent technique of analysis but not the chemical correctness of the combinations. Reference to the reacting values in the first table makes it obvious that, except by error of analysis, there can be no surplus of base or acid and that the sums must agree, no matter how the radicles are combined or whether the combinations are logical.

The disagreement between Column 1, in which sodium nitrate is computed, and Column 2, in which potassium nitrate is computed, causes several embarrassing numerical differences, and the layman understands that one analyst found saltpeter where the other did not. Though this difference may be practically unimportant some similar ones might lead to serious misunderstanding. Whether the belief is well founded that lithium is a very valuable ingredient of medicinal waters need not be discussed, but if it is desired to convey an idea of the therapeutic effect of lithium the hypothetical combinations are likely to mislead those who are not aware of the limitations of water analysis. If a water contains one part per million of lithium one can compute 5.3 parts of lithium carbonate, 6.1 parts of lithium chloride, 7.9 parts of lithium sulfate, or 9.7 parts of lithium bicarbonate. If the water had the property of causing any physiologic reaction by virtue of its content of lithium it would exert that property in proportion to its content of the lithium radicle; yet by expressing that content as lithium bicarbonate instead of the carbonate the content of lithium salts has apparently been nearly doubled and in the mind of the spring owner and his clientele, for whom these compounds are computed, the therapeutic value of the analysis, if not of the water, has been doubled.

#### INTERPRETATION OF RESULTS

In the conventional methods of interpreting the various hypothetical combinations there is general agreement in some features and disagreement in others. Table II shows the estimates of scale-forming and non-incrusting or foaming constituents that the analysts would report agree fairly well with one another, the numerical differences being too small to cause essential difference in judging the value of the water. Corresponding estimates of the amounts of soda ash and lime to soften the water would agree as closely as the sums of the constituents, because, although each analyst computes different constituents, he can not thereby change the amounts or relative proportions of the radicles with which the softening chemicals react. In deciding whether the water would be corrosive there is greater diversity of opinion. The analysts whose combinations are reported in Columns 3 and 6 apparently would state that the water is non-corrosive.

The man whose method is shown in Column 5 would doubtless report the water to be slightly corrosive, as he computes calcium nitrate. The calcium chloride indicated in Column 4 could hardly be considered corrosive in presence of so much sodium bicarbonate. In the other three statements magnesium sulfate but not calcium sulfate is reported, and there is in them no apparent reason for stating whether the water is corrosive or non-corrosive.

#### COMBINATIONS UNNECESSARY

Though hypothetical combinations are confusing and purely conventional many chemists assert that they are necessary in ascertaining the value of a water and in conveying a proper knowledge of the quality of the water.

As to the reported insistence by the lay public so-called on hypothetical combinations that can be understood it is pertinent to inquire seriously how much any series of chemical figures means to the layman and whether it is not better to report the basic facts for the information of the expert and to add interpretations of the figures for the information of those who are unable to make proper deductions for themselves. Rather intimate experience for several years with lay comments on water analyses has made me extremely skeptical as to how much of the truth hypothetical combinations convey to many men who are supposed to make practical use of the results. What the manufacturer or engineer wants to know is how a particular water will fit some use to which he wishes to put it. Is it safe to drink? Does it taste bad? Will it stain clothes? How much scale will it form in boilers? How can it be softened? Answering these questions is the function of an expert, who interprets the facts of analysis in the light of practical experience. It could be shown that hypothetical combinations are not necessary for answering these questions, though the discussion will be confined to interpretation in reference to therapeutic value and quality for boiler use.

#### MINERAL WATERS

Waters are analyzed more carefully and therefore more expensively for ascertaining their therapeutic value than for any other purpose. Mineral salts that cause definite physiologic reactions when drunk cause the reactions in relation to the radicles that are present. A solution of magnesium sulfate, for example, can be so dilute that it has no perceptible taste. An equivalent concentration of sulfate in the form of ferrous sulfate has a distinct taste, and a solution of ferric chloride containing in turn an equivalent concentration of iron has a similar taste, while again an equivalent concentration of chloride as sodium chloride has no perceptible taste. That is, in the iron solutions we taste the iron and not the sulfate or the chloride, and in order to perceive the taste of the sulfate or the chloride radicle we must use a much stronger solution of a salt whose basic radicle is comparatively weak in its effect on the organs of taste. Twenty grams of magnesium sulfate has greater laxative action than 20 grams of sodium sulfate because the magnesium ion also induces laxative action whereas

the sodium ion does not, as can be shown by an equivalent dose of sodium in the form of sodium chloride. These rather crude illustrations serve to indicate that the physiologic action of a salt is caused by one or more of the radicles composing the salt and is in proportion to their concentration. The probable cathartic effect of a sulfate water can therefore be measured by its content of sulfate, computation of the possible mathematical proportions of sodium, potassium, magnesium, and calcium sulfates being unnecessary. The cathartic action of a water is increased by its content of magnesium whether it may be possible to compute the magnesium as sulfate, chloride, or bicarbonate. As for the minor constituents of mineral waters, lithium, bromide, iodide, manganese, strontium, and the like, it would not now be necessary to combat so many fallacious ideas concerning their therapeutic value if serious consideration had heretofore been given to the concentration of these radicles instead of to the possible mathematical combinations in which they might be reported.

#### BOILER WATERS

In a very condensed article, H. Stabler<sup>1</sup> has shown how the scale-forming constituents, the foaming constituents, the tendency toward corrosion, and the quantities of softening reagents can be computed directly from the radicles without recourse to hypothetical combinations. Though it has been objected that Stabler makes the same assumptions as are made in combining the radicles as salts this is true only in so far as his formulas are based on some of the currently accepted views of the reactions that occur in boilers, concerning which much is yet to be learned; and there remains the essential difference that by use of his formulas no theoretical salts, but the estimates that are helpful to the practical man, are obtained. Comparison of the figures at the ends of the preceding tables shows that the estimate of scale directly from the radicles agrees closely with those based on combinations. All unite in including silica, iron, and aluminum as the oxides; whether there is silicate in the scale, as some have suggested, makes no arithmetical difference in the total. Magnesium carbonate and magnesium sulfate are commonly included in total scale, though magnesium is precipitated mostly as the hydrate under high-pressure conditions and the oxide better represents what is found in the scale, as in Stabler's formula. Some prefer to compute the greatest possible amount of calcium carbonate and some the greatest possible amount of calcium sulfate; calcium doubtless is precipitated in both forms and an average between them is struck in Stabler's formula.

Similarly an average is struck among the three possible sodium salts in computing the foaming constituents by multiplying sodium by 2.7. Other conditions besides the presence of a large amount of sodium salts can cause foaming, and some believe that foaming has no relation to the concentration of the sodium salts. If, however, the interpreter of an analysis believes that the sodium salts measure the

foaming tendency he gets as good estimate of that tendency by multiplying sodium by 2.7 as by computing three different salts and adding the results together.

Corrosion is considered partly a problem of reaction that involves chiefly the setting free of acids by precipitation of magnesium as the hydrate. That corrosion may be caused wholly or partly by other conditions need not concern us in discussing the practical interpretation of this theory. Stabler's formulas provide for the three possibilities. If there is not enough carbonate to combine with all the magnesium some sulfate or chloride would be set free and the water would be corrosive; under such condition those who compute hypothetical combinations report magnesium sulfate or magnesium chloride, the former of which is classed as corrosive by many analysts and the latter universally as corrosive. If there is enough carbonate to satisfy or more than satisfy both calcium and magnesium the water probably is non-corrosive; under such condition it is customary to compute all the calcium and magnesium as carbonates, to give the excess to sodium, and to class the water as non-corrosive. Thus far boiler-water analysts agree in so far as this theory of corrosion is accepted. If carbonate is sufficient to combine with calcium or magnesium alone but not with both, corrosion might or might not occur. The latter condition is that in the water under discussion, and the combinations in the second table show that various analysts calculate diversely magnesium sulfate, calcium sulfate, and calcium nitrate, and disagree as to whether corrosion would occur. The uncertainty of the corrosive action is quickly revealed by Stabler's formulas without recourse to combinations. Corrosion occurs with waters that would not be classed as corrosive by any of these calculations, but that is due to other conditions and its probability is revealed by computations of hypothetical combinations no more than by consideration of the reaction of the radicles.

#### COMBINATIONS NOT ENDORSED

Evidence of desire on the part of chemists to break away from conventional combinations of the constituents found by analysis is furnished by the resolutions adopted by various scientific organizations. As early as 1886 a committee appointed by the Chemical Society of Washington recommended<sup>1</sup> that all analyses of water should be stated in terms of the radicles found, whether elementary or combined, meaning evidently expression of the immediate results of the analysis; though this committee recommended that the combinations deemed most probable by the chemists making the analyses should also be reported it failed to recommend a manner of combination, and it is understood that the reason for lack of such recommendation is that the members of the committee could not agree on one convention.

The report of this committee was adopted<sup>2</sup> by Section C of the American Association for the Advancement of Science in 1887, and 2 years later a committee of the British Association for the Advancement

<sup>1</sup> *Eng. News*, 60 (1908), 355, also U. S. Geol. Survey, *Water Supply Paper*, 274 (1911), 165.

<sup>2</sup> *Bull. Chem. Soc., Washington*, No. 2 (1887), 35.

<sup>3</sup> *Chem. News*, 56 (1887), 113.

of Science, while agreeing with the American Association in reporting the analytical data obtained by direct determination, disapproved<sup>1</sup> the statement of the mineral ingredients combined as salts unaccompanied by the original analytical data. At the Fifth International Congress of Applied Chemistry<sup>2</sup> the discussion of two papers on methods of expressing the results of water analyses indicated that many of the chemists present favored the ionic form of statement, and at the Sixth Congress, Christomanos<sup>3</sup> recommended that the simple statement of the acid and basic radicles in parts per million be made in all water analyses. The methods of making hypothetical combinations in early editions of Fresenius's "Quantitative Analysis" are accompanied by the statement that they are general rules for which the analyst should exercise a latitude of selection.<sup>4</sup> As Fresenius's book represents to a great extent a collective opinion it is interesting to note that a recent edition omits all rules for calculating combinations, calls attention to the effect of solubility and mass action on affinity, the impossibility of comparing the reports of two analysts, and urges statement of the direct results.<sup>5</sup> A similar opinion is expressed in Tiemann-Gartner's "Handbuch der Wasser."<sup>6</sup> In this country, Handy,<sup>7</sup> McGill,<sup>8</sup> Kimberley<sup>9</sup> and several other well-known analysts have called attention to the confusing state of reports of water analyses, and Clarke<sup>10</sup> has aptly characterized hypothetical combinations as "a meaningless chaos of assumptions and uncertainties."

The figures of a hypothetically-combined water analysis express only the opinion of the man who made them, and his opinion is not only different in some respects from those of his fellow analysts but is also likely to change next year. Consequently, the statement conceals analytical facts incomparable with those concealed in other hypothetical statements, and interpretation of the data of analysis is obscured by the intervention of unnecessary combinations. In view of these facts and the apparent disinclination of the organized chemical world to approve any scheme of hypothetical combination, it seems entirely advisable for American chemists not to endorse any such convention, but to recommend simple direct uncomplicated statement of the results of analysis in ionic form.

U. S. GEOLOGICAL SURVEY  
WASHINGTON

## CHEMISTRY OF THE BLEACHING OF COTTON CLOTH<sup>11</sup>

By JOHN C. HEIDEN

Cotton fiber appears under the microscope as a twisted ribbon, thicker at the edges than in the central area. The twisted structure gives it the appearance of a spiral. The spirals, however, frequently are

reversed, so that there may be spirals turning to the right and to the left on one and the same fiber of cotton. The length of the fiber varies from  $2\frac{1}{4}$  in. for the best Sea Island to  $\frac{3}{4}$  in. for the lowest grade American cotton. The ratio of diameter to length of staple varies from 1 : 1350 to 1 : 2500. If a single fiber of low-grade American cotton were increased to a diameter of 1 in. and the length of the staple increased in proportion, the fiber would be more than 100 feet long; while if a fiber of Sea Island cotton were increased in the same proportions, the length of this staple would be more than 200 feet long. This extreme fineness, coupled with the twisted structure, makes cotton the vegetable fiber par excellence for spinning.

### COMPOSITION OF COTTON FIBER AND COTTON CLOTH

The fiber is composed of an outer layer or cuticle, a middle layer containing about 95 per cent of the total fiber substance, and a wall bounding a central canal or lumen, with substances deposited in the lumen. The cuticle serves as a varnish or waterproofing to protect the fiber, and is a mixture of fats, wax and carbohydrates, with some protein and mineral substances; the middle layer is nearly pure cellulose, while the wall of the central canal or lumen, and the compounds in the canal, are principally proteins mixed with small quantities of carbohydrates. The total substances not cellulose amount, on an average, to about 5 per cent of the fiber.

When cotton is carded and spun, practically all of the adventitious impurities are removed. To facilitate the weaving, a sizing composed of starch, fats, soaps, and frequently protein substances, is added to the warp yarn. The total additions in sizing the warp rarely exceed 5 per cent of the total weight of the fabric. Therefore, as it comes from the loom, cotton cloth, calculated on the dry weight, will contain approximately 90 per cent cellulose, 5 per cent natural impurities consisting of carbohydrates, wax, fat, protein and mineral substances, and 5 per cent of sizing material.

### COTTON CELLULOSE

Cellulose must be regarded as a definite aggregate of the products of plant life. It is a typical colloid. At the present state of knowledge it seems impossible to fix a constitutional formula, or to point to as definite reactions for cellulose or for cotton as for bodies which take the crystalline form; but from its reactions it is possible to obtain definite knowledge of its reactivity. The ease with which cellulose enters into definite combinations, as in the cuprammonium and in the xanthate or thiocarbonate reactions, and is in turn regenerated as true cellulose, shows the definite character of the aggregate and the similarity of its reactions to those of other known colloids, as for instance those of hemoglobin. Hemoglobin adds on and parts with oxygen and carbonic acid with ease, without apparently disturbing the power of the aggregate to react, and without destroying the molecule. Many other illustrations might be cited to show the definite character of the reactions of cellulose, and the similarity of these to reactions of other known colloidal molecules or aggregates. Then again the cellulose aggregate may be disturbed

<sup>1</sup> *Chem. News*, **60** (1889), 203.

<sup>2</sup> *Ber. V. Int. Kong. angew. Chem.*, **1** (1903), 261.

<sup>3</sup> *Atti del VI Cong. Int. di Chimica Applicata*, **7** (1905), 213.

<sup>4</sup> *See 2d Am. ed.*, **1896**, p. 674.

<sup>5</sup> *Cohn's Translation of 6th German ed.*, **2** (1904), 274.

<sup>6</sup> *Braunschweig* (1895).

<sup>7</sup> *Eng. News*, **81** (1904), 500.

<sup>8</sup> *Bull. Am. Ry. Eng. and Maintenance of Way Assoc.*, **6** (1905), 612.

<sup>9</sup> *Jour. Infect. Diseases, Suppl.*, **1** (1905), 157.

<sup>10</sup> *U. S. Geol. Survey, Bull.*, **330** (1908), 54.

<sup>11</sup> Presented at the 6th Semi-annual Meeting of the American Institute of Chemical Engineers, Troy, New York, June 17-20, 1914.



in its arrangement, as in the case of the formation of hydro- or oxycellulose. It will then exhibit a wider range of affinities.

On account of the colloidal nature of cellulose and of cotton, it is difficult to remove the small percentage of impurities associated with the fiber, because, like all colloidal aggregates, it readily enters into solutions or unions with other colloids. To break or purify such unions or solutions is usually a long and difficult task. For this reason one can hardly point to a chemical operation for the removal of 5 per cent of simple mechanically bound impurities which requires as many and painstaking operations as the bleaching of cotton cloth.

The cellulose molecule or pure cotton fiber reacts as a saturated compound, and has a percentage composition corresponding to  $C_6H_{10}O_5$ , and is probably a polymer of this molecule. We consider, in this investigation, that bleached cotton should be pure cellulose and that it has the above composition; we argue that, by making ultimate analyses of cloth taken from the different operations in the bleaching process, we can follow the different impurities as they are removed or eliminated from the fiber.

#### NON-CELLULOSE CONSTITUENTS OF CLOTH

If we incinerate the gray or untreated cloth we find a percentage of ash, varying from 1 per cent to  $1\frac{1}{2}$  per cent of the weight of the cloth taken. Nearly 25 per cent of the total constituent impurities are represented by this ash. Its composition averages 60 per cent compounds soluble in water, that is, carbonates, chlorides and sulfates of potassium and sodium. The remaining compounds, 40 per cent of the ash, are insoluble in water and are made up of 10 per cent to 18 per cent of the total ash of phosphates of magnesium and calcium, and the remainder of the carbonates of calcium and magnesium and the oxides of iron and aluminum.

If the cloth be treated with boiling water, 1 per cent to 2 per cent of the weight taken will be extracted, removing practically all the potassium and sodium salts, a small percentage of the calcium and magnesium compounds, and some of the fatty acids, wax and soluble carbohydrates. These latter substances are probably removed as an emulsion and not as a true solution.

Cotton, in an ultimate analysis, always gives a percentage of nitrogen and phosphorus. The Department of Agriculture, *Bulletin* 33, 1896, found, for Upland cotton, that the percentage of nitrogen varied from a maximum of 0.54 per cent to a minimum of 0.20 per cent, with an average of 0.34 per cent. These analyses cover a period of about three years. The percentage of phosphorus, calculated as phosphoric acid, varies from a minimum of 0.05 per cent to a maximum of 0.18 per cent with an average of 0.10 per cent.

#### RELATION OF THE NON-CELLULOSE CONSTITUENTS TO BLEACHING

The examination of the water extracts, the substances extracted by boiling alkalis, and the ash of cotton have been made by many investigators with

fairly concordant results. The determination of the nitrogen content has been made, not only covering American cotton as cited above, but Egyptian and Indian cotton, with concordant results. We are not, therefore, working upon an assumption if we calculate the nitrogen as a factor for determining the percentage of one constant impurity, and the phosphorus not extracted by water as another factor for determining another constant impurity. The ether and alcoholic extracts serve as checks in identifying other impurities, so that, by working from the ultimate analysis of the cloth, that is, the percentage composition expressed as carbon, hydrogen, oxygen, nitrogen, phosphorus and ash, we can arrive at accurate estimates of the percentages of the various constituent impurities removed in the different steps of the bleaching process.

The necessity of an investigation after this scheme is emphasized by the failure of the analyses of the water extracts and liquors from the kier boils to give direct evidence regarding the reactions taking place in the fiber and the amounts of the impurities removed. Then again, this method of investigation should pave the way to the discovery of the causes for much of the bad bleaching, spotted and tender goods, and other troubles met in the regular practice of bleaching cotton cloth. Frequently, cloth which has been bleached will yield colors which are clouded or streaked, particularly when dyed in light shades. The usual answer that the goods are poorly boiled is only an apology or an excuse, as it does not define in what way the boiling was faulty, whether the time was too long or too short, whether the liquor was too strong or too weak, or whether the pressure was too high or too low. When goods come from the bleach-house tender the usual explanation is that the chemick (that is the bleach liquor) or the sour (that is the acid treatment) was too strong. These answers are accepted in face of the evidence that cotton can be subjected to relatively strong solutions of bleaching powder and also to fairly strong solutions of acid without being injured. The question is not asked, how much has the cotton been changed so that its reactivity has been increased, before it was subjected to treatment with the solution of bleaching powder or with the solution of the acid? The increased reactivity of the cellulose, or cotton aggregate, when the molecule or aggregate has been disturbed, has already been referred to. In fact, the usual method given for identifying oxycellulose is based on the increased affinity of this compound for methylene blue as compared with ordinary cellulose or cotton. Cellulose is very readily hydrated and the hydroxy- and oxycelluloses are formed under many varied conditions. While these facts are recognized, there have been apparently no very serious attempts to apply them to the problems of bleaching.

#### PURPOSE AND METHODS OF BLEACHING

Cotton cloth is bleached to remove the naturally occurring brownish color, the naturally occurring impurities and the sizing material and other products added to facilitate manufacture.

Before the introduction of the use of chlorine as the true bleaching agent, cotton goods were boiled in various potash lyes, steeped in various weak acid yielding compounds, as for instance buttermilk, and then spread on bleaching greens or grass and bleached by the sun and air. Thus originated the terms "grass bleached" or "grass bleach." Bleaching on the green is still practiced today to a limited extent, in connection with chlorine bleaching, particularly for linen.

Scheele noted the bleaching action of chlorine, but Berthelot, in 1785, first suggested the use of chlorine, combined with alkali, as a bleaching agent; and shortly afterward, Watt and Tennant put the suggestion into practical operation in Glasgow.

#### AMERICAN PROCESS OF BLEACHING

The present bleaching process dates from about 1840, and is generally known as the "American process." This process consists in boiling in large kiers, with or without pressure, in solutions of lime or caustic soda, or soda ash and soaps. After the boiling process the goods are first treated with solutions of bleaching powder, then with a weak solution of acid, and then washed. The operations are varied

duration of the boiling varies for each kier boil from 6 to 14 hours, and the pressure used from atmospheric pressure to 60 pounds per square inch. A further modification of this process consists in omitting the lime boil, and substituting for the resin and ash boil, boils in a solution of caustic soda with or without the addition of resin or soap. The process then consists of the following steps:

- 1—Singeing
- 2—Steeping
- 3—Washing
- 4—First caustic soda boil
- 5—Washing
- 6—Second caustic soda boil
- 7—Washing
- 8—Treatment with solution of bleaching powder
- 9—Washing
- 10—Treatment with weak acid or souring
- 11—Washing
- 12—Drying and finishing

This process is sometimes shortened still further by using only one caustic soda boil. The time required to bleach cotton cloth varies from three to six days.

The cloth which we have examined in this investigation was taken from goods being regularly bleached

TABLE I ANALYSES OF CLOTH FROM THE VARIOUS OPERATIONS OF BLEACHING. ALL PERCENTAGES(a) CALCULATED TO DRY WEIGHT

	GRAY	STEEP	FIRST BOIL	SECOND BOIL	CHEMICK	SOUR
Carbon	43.570	40.280	43.820	37.620	41.580	44.583
Hydrogen	6.015	6.400	6.403	6.323	5.748	6.528
Nitrogen	0.191	0.192	0.020	0.016	0.015	0.014
Proteins N $\times$ 6.25	1.195	1.200	0.125	0.100	0.094	0.088
Nitrogen after ether alcohol extract	0.161	0.158				
Ash	1.198	0.333	0.103	0.055	0.085	0.061
Ash after ether alcohol extract	0.892	0.372	0.103	0.057	0.076	0.052
Ether extract	0.623	0.589	0.496	0.224	0.201	0.189
Alcohol extract after ether extract	0.782	0.326	0.214	0.230	0.231	0.151
Phosphoric acid before and after extraction	0.030	0.012	0.001	0.001	0.0013	0.001

(a) Figures are as calculated and are not rounded off.

greatly according to the quality of the goods and the requirements of finishing, etc., and may be illustrated by the following typical outlines of processes.

Madder bleach, so-called because it was used for the production of madder styles and required a very clear white for the illumination of the patterns, consists of the following operations:

- 1—Singeing
- 2—Passage through hot water to prevent the possibility of fire, and storing while wet in bins for 24 hours, usually termed "steeping" or "the steep"
- 3—Washing
- 4—Lime boil, usually under pressure
- 5—Washing
- 6—Treatment with weak acid, usually termed "souring" or "the sour"
- 7—Washing to remove this acid
- 8—Boiling in resin soap
- 9—Washing
- 10—Boiling in soda ash
- 11—Washing
- 12—Treatment with solution of bleaching powder, termed "chemicking" or "the chemick"
- 13—Washing
- 14—Treatment with weak acid to remove traces of chlorine and to further whiten the fabric, termed "the sour"
- 15—Washing, drying and finishing

This process may be modified by omitting the boiling in resin soap, and boiling instead for a longer period in a mixture of soda ash and resin soap. The

by the caustic soda boiling process, as outlined above. The samples taken and examined are numbered as follows:

- 1—GRAY—From the gray goods before singeing.
- 2—STEEP—From the goods after being washed after the singeing and steeping operation, referred to as "steep."
- 3—FIRST CAUSTIC BOIL—From the goods after being washed after the first caustic soda boil.
- 4—SECOND CAUSTIC BOIL—From the goods after being washed after the second caustic soda boil.
- 5—CHEMICK—From the goods after being washed after treatment with the chemick or bleaching solution.
- 6—SOUR—From the goods after being washed after treatment with the sour or acid. This sample represents the goods ready for finishing and printing.

#### METHODS OF ANALYSIS

Combustions were made to determine carbon, hydrogen and oxygen. The nitrogen was determined by the Kjeldahl method. The phosphorus, calcium and magnesium were determined from the ash. The ether and alcohol extracts were made, using cloth which had been dried to constant weight at 100° C. All percentages are calculated to dry weight. Table I shows the results of the analyses.

From Tables I and II we can calculate the changes produced in each operation, and follow the elimination of the various substances going to make up the constituent impurities.

TABLE II.—PERCENTAGES OF SUBSTANCES REMOVED BY EACH OPERATION AND TOTAL PERCENTAGES REMOVED AT END OF EACH OPERATION

	STEEP	FIRST BOIL	SECOND BOIL	CHEMICK	SOUR
Ash.....	70.5	{ 16.8 87.3	{ 8.1 95.4	{ 2.4 93.0	{ 2.0 95.0
Proteins.....	..	{ 91.5 14.9	{ 0.2 43.6	{ 0.5 91.7	{ 0.5 92.2
Fats and waxes.....	5.5	{ 20.4 40.0	{ 64.0 100.0	{ 67.8 100.0	{ 69.6 100.0
Phosphoric acid.....	60.0	{ 100.0	{ 100.0	{ 100.0	{ 100.0

## ACTION OF THE STEEP

The action of the steep is, in a measure, to hydrate the cotton, to allow it to take up as much water as possible. The action is slow on account of the colloidal nature of the substance. The water absorbed prepares the way for and assists the scouring action of the boil. In addition to hydrating the fiber, the steep either destroys or renders soluble about one-half of the starch of the sizing, and removes practically all of the soluble salts. By passing the cloth through a solution of malt or other diastase, after the singeing, a complete resolution of the starch into sugars or other soluble products takes place during the steeping. The quantity of diastase required is very small. The action on the starch by the ordinary steep is due to bacteria and to enzymes naturally in the cotton.

From Table II it appears that, during the steep and the wash which follows, there are removed 70.5 per cent of the constituents represented by the ash, none of the compounds represented by the nitrogen (that is, the protein substances), 5.5 per cent of the fats and waxes represented in the ether extract, and 60 per cent of the compounds represented by the phosphoric acid.

The goods, after being well washed from the steep, are taken to the boil, having been freed from the soluble impurities amounting to about one-fifth of the constituent impurities and to one-half of the added impurities if no diastase were used, and from all of the added impurities except fats when diastase is used.

## EFFECT OF VARIOUS TREATMENTS ON COTTON

Water, at ordinary temperatures, and even at temperatures corresponding to steam at 60 pounds per square inch, has no action on cotton providing air be excluded; air and steam, however, rapidly break down the fiber. In the absence of air, solutions of caustic lime or caustic soda containing as high as 10 to 20 grams per liter, are without action on the fiber, even at the highest temperatures employed in bleaching. In the presence of air, however, at relatively low temperatures, say temperatures corresponding to steam at 10 pounds per square inch, the cotton is rapidly disintegrated. Strong boiling solutions of caustic soda, say 300 grams per liter, will dissolve cotton. In boiling, that there may be no possibility of attacking the fiber, the solution should not be more than 10 grams of caustic alkali per liter, and the kier should have sufficient volume above the cloth to exclude all air. All air entrained in the pieces when packed should be allowed to escape as the temperature is raised to the boiling point, and the boil continued for a sufficient time to ensure the escape of all the air. The circulation in all bleaching kiers is from the top downward. I question therefore, whether, under these circum-

stances, all the air is ever removed from the ordinary kier.

The lime boil is not a real cleansing operation. The cloth is darker after being boiled than when in the gray. During the boiling the following reactions take place in the cloth: the starch is hydrolyzed and removed; the saponifiable fats and waxes are changed to calcium salts and remain in the fiber; there is fixed on the fiber a percentage of calcium much greater than the equivalent of the fat and wax content of the cloth. In the souring subsequent to the boil, which is always necessary after the lime boil, the calcium salts are decomposed so that the soda boils may remove the fat and waxes. The amount of calcium fixed on the fiber varies from 2 per cent to 4 per cent, expressed as carbonate.

Scheurer, in his investigation of the saponification of the fats in cotton,<sup>1</sup> found 2.88 per cent calcium carbonate after the cloth had been subjected to the lime boil, in addition to the calcium contained in the original fiber. Some observers claim the fixing of calcium to represent a true mordanting. I am inclined to believe that cotton, if in the proper condition, may fix calcium to form a calcium cellulose similar to soda cellulose. After bleaching, or some other treatments, it appears to lose this property of fixing calcium. The fact that cotton cloth which has been boiled and bleached does not produce as brilliant and clear a Turkey-red as cloth which has been simply boiled and not bleached, may be explained by assuming that the fiber is not in the proper condition to fix calcium and thus to ensure the formation of a full alizarine lake.

Scheurer, in the investigation above referred to, has shown that to saponify natural fats when boiling without pressure, the same time is required for both the caustic soda and resin boil and the lime boil; but that to saponify tallow twice as long a period is required for the lime boil as for the caustic soda and resin boil. When boiling under pressure, however, he found that the caustic soda and resin boil required twice as long a period as the lime boil to saponify both the natural fats and the tallow.

## ADVANTAGES OF SODA BOILS

The fact that cotton goods can be scoured and the fatty matters removed in sufficient quantities for the production of a good bleach by either a single boil in caustic soda and resin soap, or by a lime boil followed by a sour and another boil in soda ash lye, has turned the attention of bleachers toward the perfection of the caustic soda boil. The souring operation, which follows the lime boil, is thus eliminated, and the possibility of there being deposits of calcium salts left in the goods, on account of the imperfect souring and washing, is avoided. In the caustic soda boils, however, a good circulation of the lye must be maintained during the whole boiling operation.

## GOOD CIRCULATION OF LIQUORS NECESSARY

Scheurer, in his experiments, proved conclusively that the circulation of the liquor was absolutely necessary, and that without circulation indifferent results

<sup>1</sup> Bull. de la Société industrielle de Mulhouse.



are obtained when using either caustic soda alone or in conjunction with resin or soaps. He also found that, in the case of the lime boil followed by the sour and a soda ash boil, circulation was not important.

Kiers with a positive mechanically controlled circulation should always be used for caustic soda boils. Kiers of the ejector or injector circulating type are not to be recommended, because, in either case, the circulation is not positive. To insure a uniform action throughout the whole mass of cloth, it is the custom to boil and wash, and then repeat the boiling, so that the position of the goods is changed for the second boil. By this procedure the goods which were lying at the bottom of the kier in the first boil will lie at the top of the kier in the second boil. In this manner, a thorough penetration of the lye and uniform treatment are insured.

The saponification and removal of the fats and the destruction of the natural color, which is probably represented in the analysis by the nitrogen content, must precede the real bleaching process. If too small a percentage of the fats and color be removed or destroyed, whites which are not uniform or are not permanent, result.

#### WETTING OUT TEST FOR EFFICIENCY OF BOILING PROCESS

There is a rough test used by bleachers to determine the efficiency of the boiling process. This test consists in spotting the piece of dried goods, taken from the boiling or other process, with water, and noting the rapidity of the wetting out of the fabric. The test is best performed by cutting a piece about one inch square from the cloth, taking the precaution to have the edges cut clean and not ragged. If the edges are torn or ragged, the capillarity on the torn parts is not uniform with that of the cut edges, and the water will penetrate into the body of the fabric through the fibers longitudinally instead of transversely as when the edges are cut clean and smooth. By placing these pieces of cloth on the surface of water, it will be found that those pieces which have been thoroughly and fully boiled out sink instantly, but that those pieces which are not as well boiled out take a little longer time to sink, while pieces which have not been well boiled out float for a long time or do not sink at all.

#### ACTION OF SODA BOILS

From a study of Table I it readily appears that the boiling operation is the critical part of the bleaching process, and that in this operation the foundation is laid for the subsequent whitening operation by the action of the chlorine. Hence the dictum, "Goods well boiled are half bleached." The principal action of the caustic boils, as illustrated in Tables I and II, is on the protein bodies or nitrogen content. By the combined action of the steep and first caustic boil 91.5 per cent of the proteins are removed, and the second boil removes only 0.2 per cent more. While the boil is usually referred to as an operation for the saponification of the fats and waxes, it appears that the first function of the boil is to remove the proteins, which are almost twice as great in amount in the fiber

as the fats and waxes, as shown by the ether extract. The second function of the boil is the removal of the fats and waxes. By the combined action of the steep and the first boil 20.4 per cent of these compounds are eliminated, and the second boil removes 43.6 per cent more. It is apparent, from a comparison of these figures with the percentage representing the elimination of the proteins, that the fats and waxes are less easily removed by caustic soda, and that, after the removal of the proteins, more than twice as much of these bodies is removed in a single boil as was removed by two operations before the removal of the proteins. The fats and waxes of the cotton fiber must, therefore, contain a very large proportion of non-saponifiable matter.

The removal of 87.3 per cent of the constituents represented by the ash, and practically all of the constituents represented by the phosphoric acid, is to be noted as the result of the action of the steep and first boil, while the second boil removes 8.1 per cent more of the ash constituents.

Dr. Edward Schunk, F.R.S., in an address before The Manchester Literary and Philosophical Society, showed, from an examination of the substances removed from cotton by boiling with alkalies, that the impurities in cotton consist of the following:

- 1—Pectic acid, soluble in water, reddening litmus, and precipitated by metallic salts.
- 2—Nitrogenous colored bodies, soluble in alcohol.
- 3—Fatty acids, melting at 55.5° C., apparently margaric acid or a mixture of stearic acid and palmitic acid.

4—A wax, resembling carnauba wax, soluble in alcohol and ether; insoluble in water and caustic soda.

5—Albuminoid bodies.

The presence of the wax, described by Dr. Schunk as insoluble in caustic soda, explains the low efficiency of the caustic boil as a method for removing the fats and waxes in bleaching.

After washing from the second caustic boil, the analyses show that 91.7 per cent of the proteins are eliminated; that 64 per cent of the fats and waxes, as shown by the ether extract, are removed; that 95.4 per cent of the constituents represented in the ash are no longer in the fiber; and that all of the compounds represented by the phosphoric acid are dissolved from the cotton.

#### EFFICIENCY OF VARIOUS HYPOCHLORITES

After the washing from the boiling, the goods are treated with a solution of hypochlorite. This solution is the real bleaching agent. Bleaching powder, that is, hypochlorite of calcium, or lime chemick, as it is called, is generally used; but recently, owing to the introduction of liquid chlorine as a commercial product, hypochlorite of soda, or soda chemick, is coming to be recognized as a most convenient and reliable bleaching agent. Hypochlorite of magnesia has also been used industrially, but other hypochlorites, as for instance, zinc and alumina, have been tried only experimentally. Magnesium hypochlorite is a most excellent bleaching agent and shows no tendency to form chlorine substitution compounds; its action is

purely oxidizing. Calcium hypochlorite has a strong tendency to form chlorine substitution compounds, particularly if the solution be acid. This tendency toward substitution, in addition to its oxidizing action, is one of the drawbacks in the use of lime chemick. Sodium hypochlorite is oxidizing in its action, and has but a slight tendency toward the formation of substitution products. It is a very active bleaching solution and stands about midway, in its properties, between magnesium hypochlorite and calcium hypochlorite. Sodium hypochlorite forms no insoluble compounds, while lime chemick always fixes a percentage of calcium in the fiber. Each molecule of hypochlorous acid,  $\text{HOCl}$ , yields one atom of oxygen, which is the true bleaching agent. To treat the goods with the solution of hypochlorite, or chemick, they are saturated in a suitable machine, and piled in bins and allowed to lie for several hours, or they are floated in the hypochlorite solution for a sufficient period to produce the shade of white desired. The action of the chemick in the piling system is hastened by the carbonic acid gas in the air, while in the floating system the solution, on account of its volume, dissolves more completely and more thoroughly the colloidal substances from the fiber. The addition of weak acid, that is, acetic or formic acid, to the hypochlorite solution, to hasten the liberation of oxygen, is not to be recommended, because there is thus an increased tendency toward the formation of chlorine substitution products, particularly when lime chemick is used. The action thus becomes too rapid, no matter what kind of chemick may be used, and is not really under control.

#### ACTION OF THE BLEACHING SOLUTION AND SOURING

The permanence of the protein residue in the cloth is emphasized by the analyses after treatment with chemick. There is removed by the hypochlorite 0.5 per cent of the total proteins of the cotton, while there is eliminated 3.8 per cent of the total fats and waxes. By the combined action of the steep and the hypochlorite solution, 9.3 per cent of the fats and waxes are removed, while the first caustic boil removed only 14.9 per cent. These figures seem to indicate that these compounds are removed by mechanical action fully as readily as by chemical treatment. The ash increases from the action of the chemick, due to the fixing of calcium by the cotton. Before we treat the cloth with acid to complete the bleaching, there have been removed 92.2 per cent of the proteins, 93 per cent of the constituents represented by the ash, all of the constituents represented by the phosphoric acid, and 67.8 per cent of the fats and waxes as represented by the ether extract. The souring removes 0.5 per cent of the total proteins, 2.1 per cent of the total constituents represented by the ash, and 2 per cent of the total fats and waxes. So that the bleached cloth shows that, of the total impurities, the following percentages have been eliminated:

95.0 per cent of constituents represented by the ash.

92.7 per cent of proteins.

69.6 per cent of fats and waxes as represented by the ether extract.

100.0 per cent of substances represented by phosphoric acid.

#### WHAT IS BLEACHED CLOTH?

If we add to the percentage of the above impurities left in the cloth the percentage of the substances extracted by alcohol from the bleached cloth, we arrive at the conclusion that this piece of cloth contains 0.489 per cent of substances not cellulose. Before we accept this conclusion we must consider the fate of the carbohydrate content of the cloth. Starch would give the same percentage composition as cellulose, hence, we cannot expect to differentiate between cotton and starch in an ultimate analysis. We find, however, by qualitative tests, that starch is completely removed by diastase, or by the first caustic soda boil. The other carbohydrates, that is, the pectin bodies, are not identified in the fiber by any known method. The fate of the pectin bodies, as well as the degree of hydration of the cotton in the various operations, seem to be indeterminable.

We gain hints of what might be taking place, however, from the carbon and hydrogen relations, but I do not think we are justified in drawing any serious conclusions. I shall, therefore, leave the interpretation of the carbon and hydrogen numbers, awaiting more definite methods for determining the degree of hydration of cotton and more positive knowledge of the real pectin bodies in cotton. I, therefore, draw this conclusion, that, since the starch disappears completely, and since it is acknowledged that the pectin substances are rendered soluble and dissolved by the methods used in bleaching, it is safe to assume that we have pure cellulose if the carbon and hydrogen numbers correspond to the theoretical, allowing for a reasonable error. I think the numbers found for the goods from the sour meet such conditions.

It is to be noted that some of the original protein constituents of the fiber are soluble in ether or alcohol, or both, as shown from the extracts from the gray goods and from the goods taken from the steep, and that the hydrolyzed proteins left in the fiber after the first caustic boil are completely removed by the ether and alcohol extraction. The phosphorus content does not appear to be wholly associated with the proteins. What the real composition of the ether and alcohol extract is, and what the relation of the phosphorus is to the proteins, the fats and waxes, and to the inorganic constituents, is the subject of an investigation now in progress.

#### IMPORTANCE OF TIME FACTOR

Throughout the whole process of bleaching time is a very important element. On account of the colloidal nature of the fiber and of the impurities, it is necessary to allow the reactions to proceed slowly. For this reason bleaching cannot be hastened except with danger to the fabric. The old grass bleach, which required weeks or months as compared with our present bleaching method, requiring days, was a much more permanent and a much more beautiful bleach, because the impurities were removed slowly but completely. Therefore, it is to be recommended that all

bleaching operations be conducted in solutions. The piling of the goods, either saturated with chemick or saturated with acid, cannot be as efficient as allowing the goods to lie in solutions.

A simple test to determine whether the bleached fabric is permanent in color consists in steaming the cloth for one hour at a pressure of 5 pounds per square inch. If the color be permanent there is no change in shade, or yellowing, as it is termed; but if the bleaching be not well done or thorough, the white turns yellowish. The change of shade toward yellow, or toward the original color, serves as an index of the quality of the bleach.

#### FAILURE OF WETTING OUT TEST

The six samples analyzed, when tested by the wetting-out method described above to determine the efficiency of the boil, and by the steaming method to determine the permanence of the bleached goods, give the following results:

The gray goods and the sample taken from the steep did not sink in water, while all the other samples sank instantly. No difference in the time required for the pieces to reach the bottom of the beaker could be noted in the pieces taken from the second boil, the chemick or the sour. The piece, however, taken from the first boil required a perceptibly longer time to reach the bottom. No better illustration could be given of the failure of tests of this character to give positive knowledge. There is, in the sample taken from the first boil, 79.6 per cent of the total fats and waxes, and in the sample taken from the second boil 36 per cent, or a difference of 43.6 per cent; yet the wetting out tests show no corresponding difference.

But we must, however, note that the sample taken from the first boil showed that 91.7 per cent of the proteins are eliminated. We must also note that, after the removal of the proteins, more than twice as much of the fats and waxes are eliminated by one boil as are removed by the steep and the first boil. This raises the question, do the colloidal proteins serve as a more efficient waterproofing than the fats and waxes? When steamed, of the samples not bleached, the sample from the gray and the sample from the steep showed the same yellowing, becoming decidedly browner. The samples from the first and second boil showed the same slight yellowing, and the samples from the chemick and the sour hardly changed in tone or shade.

#### CONCLUSION

From these results we must conclude that the proteins are the cause of the yellowing of cloth in steaming, rather than the fats and waxes. Until we have positive proof that the amounts of the pectin substances present are the cause of yellowing in steaming, I think the above statement is a safe inference from the analytical results.

This investigation has been made in an effort to determine what constitutes a good bleach from a chemical standpoint. It appears from the results that such a definition is possible. It now remains to compare, by the same methods, goods not well bleached with those that are well bleached, and thus determine the definite factors.

PROVIDENCE, R. I.

### THE CHEMISTRY OF PINE OIL<sup>1</sup>

By MAXIMILIAN TOCH

One of the industries, which has developed as a result of the policy of conservation in the United States, is the manufacture of useful products from resinous woods. Enormous quantities of the latter, which in previous years were considered of little or no use and were deliberately burned in huge burners, especially constructed for the purpose, or were simply allowed to go to waste, are now being economically and profitably manipulated for the recovery of turpentine, pine oil, and rosin, or the production of tar oils, pine pitch and charcoal.

The two commercially important methods in vogue are, (1) the steam and solvent or extraction process and (2) the destructive distillation process.

Mr. H. T. Yaryan has taken out letters patent on a process for extracting turpentine and rosin from resinous woods, which very well illustrates the extraction method as practiced today. Resinous wood, reduced to fine chips by passing through a wood chipper, is charged into an iron vessel through a charging door at the top. The wood rests upon a false bottom over a coil supplied with superheated steam for producing and maintaining the proper temperature within the iron chamber. The door at the top and the discharge door at the bottom are closed, and the current of superheated steam is driven into the mass of chips. This is continued until the more volatile turpentine has been vaporized and driven over into the condensers. The wood in the extraction vessel is left charged with a small percentage of heavy turpentine, together with pine oil and rosin. Steam is shut off, the excess moisture in the hot wood is removed by connecting the vessel with a vacuum pump, and finally, a liquid hydrocarbon (b. p. 240–270° F.) is sprayed over the top and allowed to percolate down through the pores of the wood. The resinous materials are thus thoroughly and completely extracted, and passed into a storage tank, from which they are pumped into a still used for separating the component parts of the solution. From the still the hydrocarbon solvent is readily separated from the heavier pine oils by distillation under reduced pressure, on account of the great difference in the boiling point between the pine oils and the hydrocarbon solvent, the former boiling between 350–370° F. The pine oils are in turn separated from the rosin by distillation with superheated steam.

This process has been operated on an enormous scale by the Yaryan Naval Stores Company,<sup>2</sup> with plants at Brunswick, Ga., and Gulfport, Miss. This Company's Brunswick, Ga., plant alone utilizes from 500–600 tons of wood each 24 hours—probably a larger consumption than the combined pine wood destructive distillation plants of the country.

Other so-called "low temperature" processes deserve mention as possessing features of merit, although to

<sup>1</sup> Presented before the New York Section of the Society of Chemical Industry, The Chemists' Club, April 24, 1914.

<sup>2</sup> The following is a list of the Yaryan U. S. patents:

No. 913,400, March 16, 1909	934,257, September 14, 1909
915,401, March 16, 1909	964,728, July 19, 1910
915,402, March 16, 1909	992,325, May 16, 1911
922,369, May 18, 1909	



date sufficient data do not appear to be available to show their true value when operated on a large commercial scale. The Hough process, for example, is to be considered essentially a preliminary treatment in the manufacture of paper pulp from resinous woods. Chipped wood is placed in a retort and subjected to the action of a dilute alkali. The rosins are saponified and the soap separated from the alkaline liquor by cooling and increasing the alkali concentration to the desired degree. The rosin soap may be sold as such, or treated with acids for recovery of the rosin. The turpentine and pine oils are recovered either by preliminary treatment with steam or during the early stages of the cooking process.

It will be noted that in the low temperature processes the only products recovered are turpentines, pine oils and rosins, the first two removed through the action of steam, either saturated or superheated, and

distillates, in addition to tar and charcoal. This was in turn superseded by the horizontal retort, externally heated, hot gases being circulated either through an outer shell or through pipes within the retort. Next came the bath process, wherein the cordwood was immersed in a bath of hot pitch or rosin, thereby volatilizing the turpentine and lighter pine oils and dissolving the heavier oils and rosins. After this preliminary treatment the bath was withdrawn and the wood subjected to straight destructive distillation.

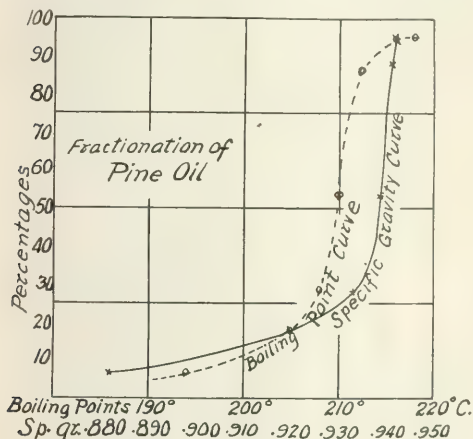
More recently<sup>1</sup> a retort has been devised utilizing the basic principle of the laboratory oil bath. The retort is heated by means of a layer of hot petroleum oil which is kept continually circulating between the retorts and an outer cylindrical shell that completely surrounds the retort proper. In this way it is claimed the temperature of distillation can be accurately controlled. The turpentine and pine oil obtained are fractionated and rectified by subsequent steam distillation. In running the retort the temperature of the oil bath is so regulated that the heat inside does not exceed 450° F., before all the turpentine and pine oil have been distilled.

The products of destructive distillation by the several processes are in each case of very much the same general nature, namely—turpentine, pine oils, tar oils, pine tar, pitch and charcoal. In some instances low grade rosin oils are also produced.

"Light Wood" does not refer to woody fiber which has a light specific gravity. The name originated from the fact that this particular wood is so rich in oil and resinous material that it is readily used for lighting fires. In the southern portion of the United States little bundles of "light wood" are for sale in strips about 1/4 in. in diameter and 1 ft. long. When a fire is applied to one of these strips of wood it becomes useful for lighting fires, hence the name "light wood." I have seen "light wood" so rich in rosins and oily material that by transmitted light a thin section looked like translucent ruby glass. It is this particular wood which is most used for the distillation of wood turpentine, pine oil and rosin.

The product from that type of pine tree from which turpentine is obtained has always been regarded as producing two materials when the sap has been collected and distilled. The one material is turpentine, and the other rosin. About ten years ago, when destructive and steam distillation of pine wood became a practical industry, a third substance was recovered. This material, intermediate between turpentine and rosin, is now known as "Pine Oil."

As far as I know, no one has yet determined the chemical constitution of this intermediate product of the pine tree, which has been designated as "Pine Oil." Two years ago I started this investigation, which is practically finished, and it is my privilege to show you to-night the raw material from which pine oil is made and the various processes by which it is refined. The chemical composition of this material and the work which led to its determination will be published, and therefore I shall not dwell at any great length on this



the latter through extraction by use of a neutral volatile solvent or a saponifying agent. The so-called "spent wood" may be used either for the manufacture of paper pulp or as a fuel to generate the power necessary to carry out the process.

In the destructive distillation process, the wood, in the form of cordwood 4' to 6' in length and 4" to 8" in diameter, is placed in a horizontal retort and the temperature gradually raised until the wood is thoroughly carbonized. The factor of greatest importance in the successful operation of this process is temperature control, as it is essential that the turpentine and pine oils be removed in so far as is possible before the temperature at which the resins and wood fiber begin to decompose is reached. The total volume of distillate as well as the percentage volume of each of the several fractions thereof, is largely dependent on the degree of temperature control.

Destructive distillation of resinous wood was first carried out in earthen trenches, the combustion being controlled by partially covering the wood with earth. Tar and charcoal were the only products recovered. Then came the beehive oven, operated in much the same crude manner, but recovering the more volatile

<sup>1</sup> T. W. Pritchard, THIS JOURNAL, 4 (1912), 338.

phase of the subject. There is as yet no standard of purity for pine oil, but that it has a definite chemical composition is now fairly well established. The only original investigation of the chemical composition of pine oil was carried out by Dr. J. E. Teeple<sup>1</sup> on "Long Leaf Pine Oil."

Dr. Teeple says: "The commercial long leaf oil, as it comes on the market, is either clear and water white, containing 3 or 4 per cent of dissolved water; or it may have a very faint yellow color and be free from dissolved water. The specific gravity ranges from 0.935 to 0.947, depending on freedom from lower boiling terpenes. A good commercial product will begin distilling at about 206° to 210°; 75 per cent of it will distil between the limits 211°–218° and 50 per cent of it between 213–217°. A sample having a density of 0.945 at 15.5° showed a specific rotation of about  $[\alpha]_D^{20} - 11^\circ$ , and an index of refraction of  $n_{1.4830}$ . In fractional distillation of the oil the specific gravity of the various distillates rises regularly with increasing temperature, becoming steady at about 0.947 at 217°.

"If the oil consists essentially of terpineol,  $C_{10}H_{18}O$ , it should be easy to convert it into terpin hydrate,  $C_{10}H_{18}O_2 + H_2O$ , by the method of Tiemann, and Schmidt.<sup>2</sup> The conversion was found to proceed easily when the oil was treated with 5 per cent sulfuric acid,

the trunk, stumps and roots of the same tree have been allowed to remain on the ground for a number of years and are then steam distilled, there is obtained, in addition to the turpentine and rosin, certain heavier oils formed by hydrolysis and oxidation as a result of exposure to the atmosphere. To the heavier oils thus formed and yielded up in the process of steam distillation the term "pine oil" is properly applied.

Pure pine oil has a very pleasant odor, an aromatic odor similar at times to the oil of caraway seed or the oil of juniper seed. When pine oil is impure it is very difficult to use it for interior work on account of pernicious odor of empyreumatic compounds. It has been used to a considerable extent for making paints which should dry without a gloss, and as a "flattening" material it has been very successful. It has the excellent quality of flowing out well under the brush and of not showing brush marks, the latter because it evaporates so very slowly. It is a very powerful solvent, and many of the acid resins which have a tendency to separate when they are insufficiently cooked with drying oils will remain together when pine oil is added. Pine oil can be used to a considerable extent as a diluent in nitrocellulose solutions, and as a cooling agent for the reduction of varnishes it also has excellent qualities. The author takes this opportunity of stating that on previous occasions his recom-

TABLE I—ANALYSES OF PINE OILS

TABLE I—ANALYSES OF PINE OILS						EVAPORATION TESTS									
Sample	Sp. gr. at 15/15° C.	Color	Acid value	Iodine value	Flash(a) point °F	ULTIMATE ANALYSES		On steam bath (b) after Per cent loss		At room temperature — 65° F Per cent loss after					
						H	O	9 hrs.	2 hrs.	4 hrs.	6 hrs.	8 hrs.	24 hrs.	32 hrs.	
S-12,200	0.9423	Faintly yellow	0.68	142.5	170	78.1	11.5	10.4	93.4	27.8	43.8	52.2	67.2	96.7	96.7
S-12,201	0.9427	Not quite water white	0.29	118.4	175	77.9	11.4	10.7	96.3	20.3	31.8	41.8	50.8	92.4	92.4
S-12,496	0.9338	Water white	0.51	125.4	145	77.0	11.1	11.9	97.3	30.4	46.9	58.6	70.0	97.5	97.5
S-14,499	0.9330	Straw color	0.59	161.5	160	81.8	10.6	7.6	93.8	...	...	...	...	...	...
S-14,500	0.9291	Pale amber	0.49	173.9	148	80.9	10.6	8.5	85.7	...	...	...	...	...	...
S-14,501	0.9355	Straw color	0.70	143.2	168	79.0	11.4	9.6	92.7	36.8	56.6	69.8	80.4	95.5	95.5
S-14,560	0.9382	Water white	0.17	139.8	175	78.4	11.2	10.4	98.6	39.5	58.9	70.5	82.5	96.5	96.5
S-14,561	0.9350	Straw color	0.73	142.7	160	79.6	11.5	8.9	95.1	46.4	68.0	81.0	88.7	94.0	94.0
S-14,562	0.9383	Water white	0.27	124.4	176	78.3	11.1	10.6	98.7	24.6	35.3	46.0	53.2	88.8	90.4
AVERAGES						79.0	11.2	9.8							

(a) Open cup (Tagliabue tester).

(b) After evaporation a small, hard residue, similar in appearance to pale rosin was left. In the case of S-14,999 and S-14,500, the residue was very dark, almost black in color, due probably to impurities in the pine oils.

either with or without admixture with benzene. If agitated continuously, the reaction is complete within 3 or 4 days. If, on the other hand, the mixture is allowed to stand quietly, the formation of terpin hydrate extends over several months and produces most beautiful large crystals, which, without recrystallizing, melt at 117–118°. When recrystallized from ethyl acetate they melt at 118°. Yield, about 60 per cent of the theoretical. This forms such a simple, cheap and convenient method of making terpin hydrate that it will doubtless supersede the usual manufacture from turpentine, alcohol and nitric acid, and instead of terpin hydrate serving as raw material for the manufacture of terpineol, as heretofore, the reverse will be the case."

"Pine oil," as now understood, is the heavy oil obtained from the fractionation of crude steam distilled wood turpentine. When the sap of the pine tree is subjected to distillation in a current of steam the volatile liquid—turpentine—consists almost entirely of the hydrocarbon, pinene,  $C_{10}H_{16}$ . When, however,

mendations concerning new and useful materials for the paint and varnish industry have been misunderstood in some instances, and it is to be hoped that this treatise will not be misinterpreted. Pine oil is a new and useful material, but it is by no means a substitute for linseed oil or turpentine or any of the other materials now on the market. It has properties peculiar to itself, and when intelligently used is of considerable value.

Practically all of the pine oil obtainable contains a small percentage of water in solution, to which it clings rather tenaciously, and it is by no means a simple matter to dehydrate this material. A rather complex apparatus for dehydrating the material is necessary with temperature control, but the test which the author has devised for the determination of water is quite simple. If 5 cc. of pine oil are mixed with 1 cc. of a neutral mineral oil, like benzene, kerosene or benzol, and a perfectly clear solution is obtained on shaking, no water is present; but if there is any water present in the pine oil the water appears as a colloid, and a milky solution is obtained which does not separate after long standing. The fact that pine oil will take

<sup>1</sup> J. Am. Chem. Soc., 30, p. 412.

<sup>2</sup> Ber., 28, p. 1781.

up a considerable quantity of water and still remain clear makes it useful for emulsion paints such as are very much in vogue at the present time for the interior of buildings, and it has been suggested that the addition of water up to 5 per cent for such a purpose is beneficial on new walls. The United States Bureau of Chemistry<sup>1</sup> has developed a method for the determination of moisture by the use of calcium carbide;

TABLE II—ULTIMATE ANALYSES

	C	H	O
$\alpha$ -Terpineol (theoretical)	77.85	11.77	10.38
French turp. (a)	87.7	11.9	...
American turp. (a)	87.7	12.1	...
Wood turp. (a)	85.7	12.1	2.2
Fine oil—first running	84.3	11.8	3.9
Distillate—pine oil, 345–380° F., 174–195° C.	82.6	11.4	6.0

(a) M. Toch, "The Chemistry and Technology of Mixed Paints," by D. Van Nostrand Company, publishers, New York.

this is being investigated at our laboratories, but on account of being a gas-volumetric method it is not quite feasible for general use in technical laboratories.

A number of commercial samples of pine oil were dehydrated and analyzed. Tables I, II and III indicate the results obtained.

Temperature	Fraction in %	Total distillate	Sp. gr., 15.5° C.
Water, 100°	2	2	
174–194	5	7	0.882
194–205	11	18	0.920
205–208	10	28	0.933
208–210	25	53	0.939
210–213	35	88	0.941
213–216	6	94	0.942
216–218	1	95	0.942
218–	4	99	

The author is glad to acknowledge here the assistance which was given him by Mr. C. A. Lunn in furnishing the samples of raw materials.

320 FIFTH AVE., NEW YORK

## OILS OF THE CONIFERAE. I—THE LEAF AND TWIG OILS OF CUBAN AND LONGLEAF PINES AND THE CONE OIL OF LONGLEAF PINE

By A. W. SCHORGER

Received July 6, 1914

The annual consumption of leaf oils of certain native conifers amounts to about \$50,000. The principal species distilled for oil are the black spruce (*Picea mariana*, Mill.), white spruce (*Picea canadensis*, Mill.), hemlock (*Tsuga canadensis*, Linn.), red juniper (*Juniperus virginiana*, Linn.), and arborvitae (*Thuja occidentalis*, Linn.). No attempt appears to have been made to distinguish between the two spruce oils and it is doubtful if much genuine hemlock oil is to be found on the market, since the oils of the three species are quite similar and for practical purposes no distinction seems necessary. Fritzsche Brothers of New York City estimate the annual consumption of spruce oil at 40,000–50,000 pounds. It is extensively employed as a perfume in greases and shoe-blackings and is quoted at \$0.45–\$0.60 per pound. The leaf oil of the red juniper is sold at about the same price as spruce oil, and is largely used in insecticides. The annual consumption is 15,000–20,000 pounds.

The annual cut of lumber from conifers far exceeds that of the hardwoods. The tops are left in the woods and, in addition to being a total loss, are the most fruitful source of forest fires. Several states have

attempted to cope with the fire problem by passing laws compelling either the "lopping" or burning of the tops. The Forest Service in leasing timber rights stipulates that the tops must be burned or lopped and scattered. If only sufficient oil could be obtained to pay for the cost of handling the material, there would be an economic gain to the lumberman, since lopping or burning entails an expense with no return whatever for the labor involved.

This investigation was undertaken with a view to determining the yield and composition of the leaf oils of the more important conifers with a view to their utilization.

Several western species were distilled by Mr. G. M. Hunt of the Forest Service. The yields obtained for these oils and their composition will be published later. In most cases the yields from the western species were low. The odor of the oils from both the western and southern species was peculiar and less pleasant than the spruce oil of commerce. This may be accounted for by their low alcohol and ester content compared with spruce oil. From the yields of oil obtained from the southern and western species it was thought that an approximate idea of the probable yield of a species could be obtained from the cross section of the needles. The inference is logical that the yield should depend on the number and size of the resin ducts per unit of cross sectional area. Cross sections of the needles of several species were made and the above inference was verified in a striking manner, as will be noted by reference to Figs. 1, 2, and 3.

**APPARATUS**—The still proper was constructed in three parts (Fig. 4). The cylindrical body of the still for holding the needles was 3 feet 6 inches in height by 2 feet 3 inches in diameter, made of No. 16 B. W. G.<sup>1</sup> copper. The ends were flanged out and attached to iron rings 1<sup>3</sup>/<sub>4</sub> inches wide. The covers of the still and of the heating vessel were similarly flanged and provided with rings. The top and base were clamped to the cylinder by 2<sup>1</sup>/<sub>2</sub> inch malleable iron clamps. Asbestos wire tape was used in these make and break joints. The inner base of the cylinder was furnished with lugs upon which rested a frame covered with 20 mesh No. 25 B. W. G. brass wire to support the needles. To reduce radiation and resultant condensation of the vapors the cylinder was covered with asbestos. The heating vessel was 3 feet in diameter by 2 feet 1 inch high and constructed of No. 16 B. W. G. copper except the bottom, which was No. 11 B. W. G. copper. The heating vessel was supplied with a 4<sup>1</sup>/<sub>2</sub> inch funnel provided with a lever handle stop, and a 1<sup>1</sup>/<sub>2</sub> inch water gauge.

An 8 foot copper pipe, in two sections, two inches in diameter, connected the cover with the condenser. The latter consisted of 20 feet of 1<sup>1</sup>/<sub>4</sub> inch copper tubing wound in a coil of 1<sup>1</sup>/<sub>2</sub> feet internal diameter. The coil was placed in a galvanized iron tank 2 feet in diameter by 2<sup>1</sup>/<sub>2</sub> feet deep. The receiver (Fig. 5) consisted of a 2 gallon aspirator bottle furnished with a brass siphon. During distillation the receiver was

<sup>1</sup> U. S. Dept. Agric., Bur. Chem., Circ. 97.

<sup>1</sup> Birmingham wire gauge.



covered with wet burlap as a protection against the sun's rays.

**PREPARATION OF MATERIAL**—The cones of the longleaf pine distilled were very green and pulpy, only the prickles being colored brown. They were mashed previous to distillation.

The twigs and needles were run through a feed cutter driven by hand. By twigs is meant the woody portions of the limbs  $\frac{1}{2}$  inch or less in diameter.

One run of needles only was made for each species. They were stripped from the twigs by hand. This selection of material did not appear to materially raise the quality of the oils.

When the knives were kept sharp, the majority of

half filled with water and the fire started. By filling the cylinder with needles ahead of the rising column of steam they are rendered decidedly more compressible. The average content by charging the needles in the cold was 350 pounds, while by filling ahead of the steam the charge was increased to 400 pounds. The distillate appeared at the outlet of the condenser in 2 to 3 hours after the fire was lighted and the distillation was continued at the rate of 2.5 gallons of distillate per hour. When the quantity of oil distilling per hour fell to 5 to 6 cc. per hour the distillation was considered complete. This was reached in 7 to 8 hours. At intervals the distillation water from the receiver was returned to the boiler. The exhausted needles were dumped

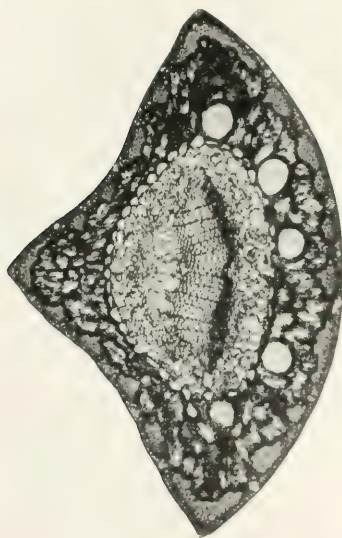


FIG. 1

1—Longleaf Pine (*Pinus palustris*)  
5 large oil ducts—average yield of oil,  
0.401 per cent.



FIG. 2

CROSS SECTIONS OF PINE LEAVES  $\times 150$   
2—Cuban Pine (*Pinus heterophylla*)  
10 small oil ducts—average yield of oil,  
0.271 per cent.

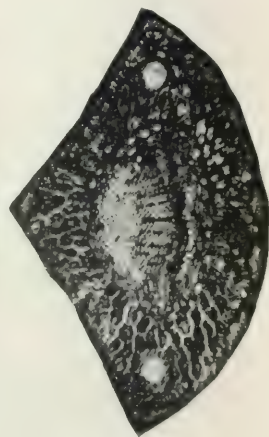


FIG. 3

3—Western Yellow Pine (*Pinus ponderosa*)  
2 oil ducts—average yield of oil,  
0.112 per cent.

the material was obtained in lengths of one-half to one inch. The comminution of the material has three advantages as follows:

- 1—Oil distills from the needles more rapidly
- 2—Increased yield of oil
- 3—More material can be placed in the still

The beneficial effect of fineness of material in increasing the yield of oil and speed of distillation are obvious, and in addition to the mechanical effect of exposing the oil ducts, the finer material can be so packed as to prevent "channeling." With entire needles and twigs uniform packing can not be secured in a small still, with the result that channels are formed and a portion of the material escapes the action of the steam to a greater or less extent. An increase of 25 to 50 per cent more chopped material can be placed in the still than when left in the original state.

**DISTILLATION PROCEDURE**—The boiling vessel was

from the cylinder by means of a pole furnished with a rope that attached to handles on the cylinder (Fig. 4). The oil from the receiver was dried, filtered, and weighed, and the percentage yield based on the weight of material in the charge.

The oils discussed in this paper were distilled in June, 1912, on the Florida National Forest.

#### LEAF AND TWIG OIL OF CUBAN PINE (*Pinus heterophylla*, Ell.)

THE PHYSICAL AND CHEMICAL CONSTANTS OF THE OILS

Sample	Specific gravity 15° C.	Refractive index 15° C.	Optical rotation 20° D.	Acid No.	Ester No.	Yield of oil
2797	0.8877	1.4869	-35.67°	0.65	9.73	0.269
2798	0.8894	1.4852	-33.41°	0.75	10.37	0.268
2799	0.8885	1.4845	-32.09°	0.66	10.01	0.278
2800	0.8878	1.4845	-34.83°	0.71	10.54	0.268
			Mean	0.69	10.16	0.271
2801(a)	0.8895	1.4880	-36.54°	0.78	8.75	0.193

(a) Oil from needles only.

FRACTIONAL DISTILLATION OF OIL OF CUBAN PINE	
Boiling point, ° C.	Per cent
159.0-165.0	31.0
165.0-170.0	18.0
170.0-180.0	7.0
180.0-197.5	3.0
197.5-250.0	16.0
250.0-280.0	18.5
Residue	6.0

**FURFURAL**—The first fraction was shaken out with water. The aqueous solution gave an intense rose-red color characteristic of furfural when treated with aniline and hydrochloric acid. This aldehyde has been found to be a constant constituent of leaf oils and is probably formed by the decomposition of ligneous material during distillation.

**$\alpha$ -PINENE**—After repeated fractionation 19.65 grams (3.93 per cent) of oil distilled between 156-160°. It had the following properties:  $d_{15}^4$ , 0.8655;  $\alpha_{D25}^4$ , -31.39°. Fifteen grams of the oil gave but 1.4 grams of pinene nitrosochloride by Wallach's method.<sup>1</sup>

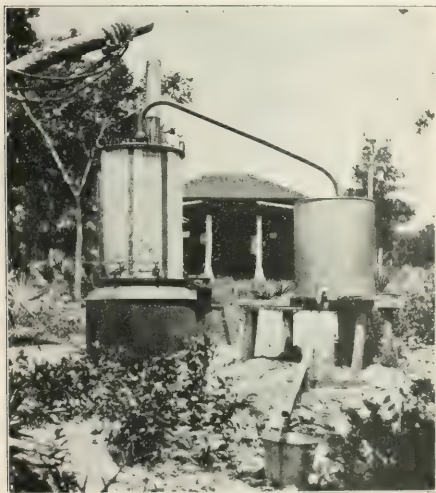


FIG. 4—STILL AND CONDENSER

The nitrosochloride melted at 98-99°; its nitrol-piperidine compound at 117-118°.

**CAMPHENE**—Two camphene fractions were collected as follows: (1) 31.8 grams, b. p. 160-161°;  $d_{15}^4$ , 0.8666;  $\alpha_{D24}^4$ , -30.35°; (2) 18.8 grams, b. p. 161-162°;  $d_{15}^4$ , 0.8676;  $\alpha_{D24}^4$ , -28.81°. These fractions were hydrated by the method of Bertram and Walbaum<sup>2</sup> and saponified. The oily product obtained was distilled and the portion boiling below 190° rejected. The residue, on cooling, solidified to a crystalline mass. The crystals purified by means of a force filter and crystallization from petroleum ether melted at 209-210° in a sealed tube. Five grams of the isoborneol were oxidized with acetic and chromic acids on the water bath and 2 grams of camphor obtained. The semicarbazone melted at 235-236°.

**$\beta$ -PINENE**—The total  $\beta$ -pinene fractions, b. p. 162-170°, weighed 176.8 grams (35.4 per cent). The

portion, b. p. 164-166°, had the following constants:  $d_{15}^4$ , 0.8704;  $\alpha_{D25}^4$ , -24.12°. After oxidation of the oil with alkaline permanganate solution by Wallach's method<sup>1</sup> 10.25 grams of crystalline sodium nopinate were obtained for 33.65 grams of oil actually oxidized. The free nopinic acid melted at 125°. A portion of the sodium nopinate was oxidized to nopinone and converted to the semicarbazone. This compound melted at only 185-186° after six crystallizations from alcohol.

**DIPENTENE**—After repeated fractionation 41.5 grams (8.3 per cent) boiled between 170-180°. The portion, b. p., 170-184°,  $\alpha_{D25}^4$ , -23.10°, was examined for phellandrene with negative results. An ether solution of this fraction on saturation with dry HCl gas, yielded a dihydrochloride, m. p. 49°. The oil, b. p. 174-178°, yielded a tetrabromide, m. p. 115-117°. The dipentene tetrabromide probably contained some of the active compound.

**BORNEOL**—The fraction of the oil, b. p. 197.5-250°, was saponified and the recovered oil heated with an equal weight of phthalic anhydride in an oil bath at 150-160° for four hours. The reaction product was treated with dilute sodium carbonate solution to convert the acid phthalic ester to the soluble sodium salt, and repeatedly extracted with ether to remove the unchanged phthalic anhydride and neutral oils. On saponification of the sodium salt of the ester and simultaneous steam distillation solid borneol was obtained. After recrystallization it melted at 201-202°. A 20.4 per cent alcoholic solution showed the rotation  $\alpha_{D25}^4$ , -2.99°.

The acids obtained from the original saponification of the ester fraction were converted to their sodium salts and precipitated with  $\text{AgNO}_3$  in two fractions. Analysis of the silver salts follows:

Grams of silver salt	Grams of silver found	Percentage silver
0.2149	0.0954	44.39
0.1455	0.0684	47.01

The silver salts of caprylic and caproic acids require 43.0 per cent and 48.4 per cent of Ag, respectively, and it is probable that the above precipitates represent a mixture of the two salts.

**CADINENE**—The oil boiling between 250-280° was fractionally distilled over metallic sodium and 35.3 per cent obtained boiling between 270-280°. It has the following properties:  $d_{21}^4$ , 0.9190;  $\alpha_{D21}^4$ , +14.76°. The oil was dissolved in ether, saturated with HCl gas



FIG. 5 RECEIVER WITH SUPERNATANT LAYER OF OIL

<sup>1</sup> *Annalen*, **245** (1888), 251; **263** (1889), 251.

<sup>2</sup> *J. prakt. Chem.*, **49** (1894), 1.

<sup>1</sup> *Annalen*, **356** (1907), 228.

and allowed to stand twelve hours in a cool place. On evaporation of the ether a crystalline residue remained. These crystals after washing with alcohol and recrystallizing from ethyl acetate melted at  $118^{\circ}$ . An 11.3 per cent ether solution of the cadinene dihydrochloride had the rotation  $\alpha_{D21} = -3.51^{\circ}$ .

#### LEAF AND TWIG OIL OF LONGLEAF PINE

(*Pinus palustris*, Mill.)

##### PHYSICAL AND CHEMICAL CONSTANTS OF THE OILS

Sample No.	Specific gravity 15° C	Refractive index 15°	Optical rotation $\alpha_{D20}$	Acid No.	Ester No.	Ester after acetylation	Per cent yield of oil
2802	0.8829	1.4825	-29.09	0.55	7.22	36.53	0.429
2803	0.8844	1.4818	-26.38	0.69	6.64	42.77	0.381
2804	0.8836	1.4819	-29.79	0.73	6.05	46.37	0.412
2805	0.8849	1.4824	-30.49	0.68	7.08	43.18	0.382
			Mean 0.66	6.75	42.21	0.401	

##### FRACTIONAL DISTILLATION OF OIL OF LONGLEAF PINE

Boiling point, °C	Per cent
158.0-165.0	38.0
165.0-170.0	25.0
170.0-180.0	5.0
180.0-198.5	2.0
198.5-250.0	16.0
250.0-280.0	10.7
Polymerized residue	3.0

**FURFURAL**—The aqueous extract of the first fraction gave a good color reaction for furfural with aniline and hydrochloric acid.

**$\alpha$ -PINENE**—After nine fractional distillations 42.8 grams (8.6 per cent) distilled between  $156$ – $160^{\circ}$ . The fraction tested for  $\alpha$ -pinene had the following constants: B. p.,  $156$ – $158^{\circ}$ ;  $d_{15}^{\circ}$ , 0.8661;  $\alpha_{D21}$ ,  $-13.47^{\circ}$ . Ten grams of this fraction, yielded 2.21 grams of pinene nitrosochloride. The latter body was transformed to the nitropiperidine melting at  $119^{\circ}$ .

**CAMPHENE**—The following fractions were examined for camphene: (1) b. p.,  $160$ – $162^{\circ}$ ;  $d_{15}^{\circ}$ , 0.8686;  $\alpha_{D17}^{\circ}$ ,  $-15.28^{\circ}$ ; weight, 51.3 grams; (2) b. p.,  $162$ – $163^{\circ}$ ; weight, 16.2 grams. The fractions treated by the method of Bertram and Walbaum yielded about 10 per cent of their weight of solid isorneol. After repeated crystallizations from petroleum ether the product melted at  $207$ – $210^{\circ}$ . The low melting point may be explained by the fact that by this method of identification some borneol is usually formed along with the isorneol.

**$\beta$ -PINENE**—Two hundred grams (44.0 per cent) of oil were finally obtained boiling between  $163$ – $170^{\circ}$ , the major portion boiling between  $164$ – $166^{\circ}$ . The fraction with the latter boiling point had the constants:  $d_{15}^{\circ}$ , 0.8724;  $\alpha_{D21}^{\circ}$ ,  $-17.96^{\circ}$ . One hundred grams of oil were oxidized by Wallach's method. By steam distillation 53.3 grams of oil were recovered. The oxidation liquors yielded 13.15 grams of crystalline sodium nopolate. The free nopinic acid melted at  $126$ – $127^{\circ}$ . On oxidizing 8.85 grams of sodium nopolate with 3 grams of potassium permanganate and 2 grams of sulfuric acid, 2.24 grams of nopinone were obtained. The nopinone semicarbazone melted at  $187^{\circ}$ .

**DIPENTENE**—The oil boiling finally between  $170$ – $180^{\circ}$  weighed 24.8 grams. The optical rotation of the fractions b. p.  $170$ – $174^{\circ}$  and  $174$ – $180^{\circ}$  were:  $\alpha_{D17}^{\circ}$ ,  $-21.85^{\circ}$  and  $-22.97^{\circ}$ , respectively. Phellandrene was not detected and the crystalline dihydrochloride obtained melted at  $50^{\circ}$ , indicating the absence of

sylvestrene. By brominating a portion of the oil a tetrabromide melting at  $124^{\circ}$  was obtained.

**BORNEOL**—The fraction b. p.  $198.5$ – $250^{\circ}$  was saponified and the oil recovered by steam distillation. The portion boiling in the neighborhood of borneol had a rotation  $\alpha_{D28}^{\circ}$   $-37.17^{\circ}$ . By means of its phthalic ester borneol, m. p.  $201$ – $202^{\circ}$ , was obtained. The borneol was then oxidized to camphor whose semicarbazone melted at  $231$ – $233^{\circ}$  after two crystallizations from alcohol. Lack of material prevented further recrystallization.

The acids obtained by saponification of the esters were accidentally lost but there is no reason to expect a difference from the acids of the leaf oil of this species, the analysis of which will be found below.

**CADINENE**—The sesquiterpene fraction b. p.  $250$ – $280^{\circ}$  and weighing 53.6 grams (10.7 per cent) distilled mainly between  $260$ – $270^{\circ}$ . The portion with the latter boiling point had the specific gravity  $d_{15}^{22}^{\circ}$ , 0.9185 and optical rotation  $\alpha_{D22}^{\circ}$   $+6.82^{\circ}$ . On treatment with HCl gas a dihydrochloride, m. p.  $117$ – $118^{\circ}$ , was obtained in large quantity. An 8.37 per cent ether solution of the crystalline dihydrochloride had a rotation  $\alpha_{D26}^{\circ}$   $-2.85^{\circ}$ .

#### LEAF OIL OF LONGLEAF PINE

One charge of needles that had been separated from the twigs by hand yielded, on distillation, 0.417 per cent of oil having the following properties:  $d_{15}^{\circ}$ , 0.8841;  $n_{D15}^{\circ}$ , 1.4834;  $\alpha_{D28}^{\circ}$ ,  $-32.50$ ; acid No., 0.67; ester No., 5.91; ester No. after acetylation, 40.46. The ester numbers are equivalent to 2.07 per cent ester calculated as bornyl acetate,  $C_{10}H_{17}.OOC.CH_3$ , and 9.75 per cent. of free alcohol,  $C_{10}H_{17}.OH$ , calculated as borneol.

Chemical analysis showed the same constituents to be present as in the leaf and twig oil above. It was anticipated that the leaf oil would show a greater alcohol and ester content than the leaf and twig oil and a correspondingly less terpene content. In fact, however, as calculated from the ester numbers after acetylation, the leaf oil showed a total alcohol content, as borneol, of 11.38 per cent, while the average total alcohol content of the leaf and twig oils was 11.88 per cent. As is well known, the oil from the wood of this species consists largely of  $\alpha$ -pinene. The leaf oil should accordingly contain less  $\alpha$ -pinene than the leaf and twig oil. In so far as fractionation is of value in quantitative determination this assumption was true.

The acids obtained by saponification of the esters were recovered in the usual way and precipitated in two fractions with  $AgNO_3$ . The silver salts were analyzed as follows:

No.	Grams of silver salt	Grams of silver found	Percentage silver
1.....	0.0638	0.0274	42.95
2.....	0.0871	0.0406	46.61

The silver salts of caprylic, heptioic, and caproic acids require 43.0, 45.5, and 48.4 per cent Ag, respectively. The first fraction agrees with silver caprylate and the second fraction probably consists of a mixture of the silver salts of caprylic or heptioic acid with caproic acid.



## CONE OIL OF LONGLEAF PINE

The green cones yielded 0.363 per cent of oil having the following properties:  $d_{15}^4$ , 0.8756;  $n_{D15}^{20}$ , 1.4760;  $\alpha_{D28}$ ,  $-9.22^\circ$ ; acid No., 0.42; ester No., 3.95; ester No. after acetylation, 31.07. The oil had a disagreeable odor that was especially pronounced in the first fraction on fractionation. This odor resembled the higher aldehydes of the aliphatic series.

## FRACTIONAL DISTILLATION OF CONE OIL OF LONGLEAF PINE

Boiling point, ° C.	Per cent
155.0-160.0	11.0
160.0-165.0	61.0
165.0-170.0	11.0
170.0-180.0	3.5
180.0-195.5	1.5
195.5-250.0	8.3
250.0-275.0	1.2
Residue	2.3

**FURFURAL**—A qualitative test showed furfural to be present in the first fraction.

**$\alpha$ -PINENE**—The total  $\alpha$ -pinene fractions, b. p. 156–160°, weighed 193 grams (39.6 per cent). The fraction b. p. 156–158°,  $d_{15}^4$  0.8637,  $\alpha_{D28}$   $+6.82^\circ$ , gave an excellent yield of pinene nitroschloride. Its nitrol-piperidine compound melted at 118–119°. It will be noted that the  $\alpha$ -pinene fraction from the cone oil is *d*-rotatory, while that from the needle oil was *l*-rotatory.

**CAMPHENE**—The fractions examined for camphene were as follows: (1) 30.85 grams, b. p. 160–161°,  $d_{15}^4$  0.8671,  $\alpha_{D28}$   $-0.31^\circ$ ; (2) 28.6 grams, b. p. 161–162°,  $d_{15}^4$  0.8685,  $\alpha_{D28}$   $-3.41^\circ$ . By treatment with glacial acetic and sulfuric acids isoborneol, m. p. 208–210°, was obtained.

**$\beta$ -PINENE**—A total of 125 grams (25 per cent) boiled between 162–170°. The major portion, b. p. 164–166°, had:  $d_{15}^4$  0.8714;  $\alpha_{D28}$ ,  $-11.80^\circ$ . By oxidation with alkaline permanganate a yield of 26.8 per cent of crystalline sodium nopinate was obtained. The free nopinic acid melted at 125–126°.

**DIPENTENE**—In the oil b. p. 170–180° phellandrene could not be detected. By treatment with dry HCl gas the dihydrochloride obtained melted at 49–50°. The fraction b. p. 174–180°, and having a rotation  $\alpha_{D28}$   $-18.24^\circ$ , yielded dipentene tetrabromide melting at 123–124°.

**BORNEOL**—The fraction b. p. 195.5–250° was saponified and the recovered oil heated with phthalic anhydride. By the customary procedure borneol, m. p. 202–203°, was obtained. An alcoholic solution of the borneol was *l*-rotatory.

**CADINENE**—The highest boiling fraction contained the sesquiterpene cadinene. The crystalline dihydrochloride melted at 116–117°. A 3.34 per cent of the hydrochloride in ether gave a rotation  $\alpha_{D28}$   $-1.18^\circ$ .

## SUMMARY

The several oils of the two species examined are practically identical in composition. The same constituents, in varying percentages, were found in each. The compositions of the oils and the approximate percentages of the constituents are shown in the following table.

The combined borneol in the leaf and twig oil of the Cuban pine probably occurs as the esters of caproic and caprylic acids; that in the leaf oil of longleaf pine as the esters of caprylic, heptioic, and caproic acids.

The rotation of the cadinene as given above must be accepted with certain reservations. While the sesquiterpene fractions were *d*-rotatory, their dihydro-

## PERCENTAGE COMPOSITIONS OF PINE OILS

	CUBAN		LONGLEAF	
	Leaf and twig	Trace	Leaf and twig	Leaf
Furfural	Trace	Trace	Trace	Trace
<i>l</i> - $\alpha$ -Pinene	4	8-9	5	39-40a
<i>l</i> -Camphene	10	13-14	12-13	12
<i>l</i> - $\beta$ -Pinene	35-36	44	50	25
Dipentene	8	5	5	6-7
Bornyl ester (as acetate)	3.5	2.4	2	1.4
Free alcohol (as <i>l</i> -borneol)	11.4	10.0	9.8	7.6
<i>d</i> -Cadinene	18-19	10-11	11	1-2
Losses by polymerization, etc.	9	6.0	7.5	6.5

(a) *d*- $\alpha$ -pinene.

chlorides were all *l*-rotatory. The only oil containing *d*-rotatory cadinene whose dihydrochloride was likewise *d*-rotatory, as recorded in the literature, is that of Atlas cedar and possibly also West Indian sandalwood oil.<sup>1</sup>

FOREST PRODUCTS LABORATORY  
FOREST SERVICE, U. S. DEPARTMENT OF AGRICULTURE  
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## THE SPECIFIC HEAT OF CALIFORNIA PETROLEUMS

By HAROLD E. WALES

Received May 11, 1914

The following work was carried out at the University of California under the direction of Prof. E. O'Neill. It was intended to furnish those interested with data on the available oils and their specific heats.

**METHODS**—Two methods were employed: (1) The use of an electric method; (2) the application of a modified form of Regnault's calorimeter.

The electric method consisted in using the ordinary form of an electric lamp as a source of heat. The lamp was immersed in the oil which was placed in a calorimeter cup and the current turned on; the rate of rise in temperature was measured and by comparison with the rate of rise of a similar weight of water the specific heats were calculated.

The apparatus used in the modified Regnault method consisted of a Dewar flask which was surrounded by an insulated container and in which the oil was placed. A brass or metal weight was heated in a condenser by means of steam and then dropped in the oil, the rise in temperature of the oil being measured. By means of the formula below the specific heats were calculated:

$$c = \frac{M(T - t)}{Cm(t - t_0)} \frac{W}{m}$$

where  $W$  = water equivalent of the apparatus

$m$  = mass of oil

$c$  = specific heat of the oil

$C$  = specific heat of the brass or metal weight

$M$  = weight of the brass or metal weight

$T$  = initial temperature of the weight

$t_0$  = initial temperature of the oil

$t$  = final temperature of the oil.

The electric method was found to be the least sensitive of the two, results checking within about 2 to 5 per cent. In the case of the modified Regnault method the accuracy very often approached 1.5 per cent.

<sup>1</sup> Gildemeister and Hoffman, "The Volatile Oils," 1 (1913), 330.

RESULTS—Twelve samples of oil were used. They were tested for water, low fractions and asphalt. The results of the analysis of these oils as well as the specific heats found are given below.

Sample No.	Water	DISTILLATE PERCENTAGES				Specific heat at 20° C.
		0-150° C.	150-300° C.	300° C.	Asphalt	
1.....	0	0	.....	.....	.....	0.3999
2.....	0	33	.....	.....	.....	0.4143
3.....	0	52	.....	.....	.....	0.4389
4.....	7	0	5.7	23.14	32.1	0.5016
5.....	1.3	0	37.4	30.0	30.91	0.4788
6.....	0	35.6	54.1	4.2	6.2	0.4804
7.....	0	8.1	37.3	39.7	23.8	0.4474
8.....	0	25.8	43.3	22.1	7.0	0.4832
9.....	0	0	12.3	48.7	36.3	0.4419
10.....	0	0	22.6	42.3	34.7	0.4553
11.....	6.2	0	30.9	22.6	39.9	0.4559
12.....	0	0	34.1	30.2	35.4	0.4491

From the above results it can be seen that the average specific heat of California petroleum is around 0.4500. The oils 1, 2 and 3 were oils containing only the fractions from 300° C. up. The results show that as the asphalt content increases the specific heat decreases while as the water content increases the specific heat increases.

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#### DETERMINATION OF SILVER AND BASE METAL IN PRECIOUS METAL BULLION

By FREDERIC P. DEWEY

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(Concluded from the August Number)

##### THE DIRECT DETERMINATION OF SILVER

The determination of silver in solution by titration with a solution of sulfocyanate was described by Volhard in *Jour. prakt. Chem.*, in 1874, and is generally spoken of as the "Volhard method," but priority has been claimed for Charpentier, based upon publications in *Compt. rend.*, in 1871, and *Bull. Soc. Ing. Civ. de France*, in 1870.

In general, the method consists in adding a liberal amount of a ferric salt to the silver solution and then adding from a burette a solution of a sulfocyanate of a convenient strength, finishing drop by drop, until the characteristic red color of the ferric salt with sulfocyanate appears. More or less elaborate descriptions of it will be found in various text-books.

When working upon high-grade silver, 992 fine or over, this method probably yields fully as accurate results as the Gay-Lussac method (titration with salt solution). No special apparatus is necessary and when only a few determinations are required it is more rapid than the Gay-Lussac method. The chief advantage of the Gay-Lussac method is its ability to turn out, with proper equipment, a larger volume of work in a day's time.

When, however, the Volhard method is applied to miscellaneous materials some objections appear. Mercury and palladium interfere. Moderate amounts of copper and platinum are not objected to. It is often said that 70 per cent of copper may be present, but this is certainly a mistake. Nickel and cobalt obscure the end color. It has been suggested when Ni and Co are present to add excess of sulfocyanate and titrate back with silver. Chloride of silver must be absent since it gradually reacts with sulfocyanate

in solution. Lower oxides of nitrogen must be absent. Ferrous iron, in presence of nitric acid, must not be used as the indicator since this would mean lower oxides of nitrogen. It should be noted that ferric sulfate as indicator may cause precipitation of lead sulfate when the bullion contains lead. It has been recommended to use two solutions, a standard and tenth standard.

In dissolving bullion carrying tin in nitric acid, purple of Cassius is almost always formed and this interferes most seriously in determining the sulfocyanate end point. Stanniferous bullions are quite rare, but one office gets placer gold bars carrying tin occasionally, and another gets scrap bullion containing tin at intervals.

When the amount of silver present is known approximately and the equipment is at hand, it has been recommended to precipitate nearly all the silver with standard salt solution and finish the titration with sulfocyanate. The necessity of separating the AgCl from the solution before adding the sulfocyanate makes this combination method too lengthy.

When we take up the question of applying this method to the determination of the silver present in gold bullion, we are at once confronted with the problem of getting the silver into solution. Where the bullion is less than 300 fine in gold, possibly the other metals may be directly dissolved in nitric acid, but above that gold fineness, some preliminary treatment is necessary.

In order to make a satisfactory determination of silver in bullion carrying Pt, it was the practice at the Philadelphia Mint, for many years previous to 1890, to alloy with Pb on a cupel, removing from the muffle as soon as thorough alloying was secured. The cold button was cleaned and then treated with nitric acid. The alloying required considerable care and skill and there was often trouble from the separation of lead nitrate if strong acid was used. The silver in the solution was determined by the Gay-Lussac method.

Primarily for the determination of the gold, G. Rose<sup>1</sup> proposed to alloy with lead in a porcelain crucible over a spirit lamp, Jüptner<sup>2</sup> alloyed with zinc and Balling<sup>3</sup> with cadmium. In all of these cases the solution was available for determining the silver; in fact, Rose proposed to precipitate the silver by solution of chloride of lead.

In 1891, Dr. Cabell Whitehead,<sup>4</sup> then Assayer of the Bureau of the Mint, described the use of the cadmium fusion for the determination of silver in gold bullion, particularly when present in very small amounts as in gold coins, but he regards the determination of gold by this method unfavorably.

In the Annual Report of the Director of the Mint for 1912, page 33, Mr. M. A. Martin, the Assayer of the San Francisco Mint, has proposed the following method of determining silver in mass melts combining a number of deposits:

<sup>1</sup> Mitchell's "Manual of Practical Assaying," 1881, p. 688

<sup>2</sup> *Z. anal. Chem.*, 1879, p. 105.

<sup>3</sup> Crookes' "Select Methods of Chemical Analysis," 1886, p. 443.

<sup>4</sup> *Proc. Franklin Inst.*, 1891, III, p. 94.

# THE DETERMINATION OF SILVER IN MASS MELTS OF GOLD BULLION

"For several years past we have experienced no little difficulty in the endeavor to determine correctly the silver content of gold bullion mass melts by means of cupellation, the many varieties of alloy usually present in bullion of this character rendering it almost impossible to obtain a close agreement between duplicate assays.

"Early in the fiscal year we experimented with a different method, the results of which have been so satisfactory as to justify its permanent adoption. The details of the process are as follows:

"A scorifier about two-thirds full of 98 per cent potassium cyanide is placed in the front of the muffle furnace, care being taken that the contents are kept below the boiling point. The assay is weighed up at 1000 gold weight, wrapped in a small sheet of lead foil weighing about one gram and immersed in the molten cyanide. A piece of stick cadmium weighing approximately five grams is immediately added, and by a slight rotation of the scorifier is brought into contact with the bullion sample. The metals unite rapidly, a complete alloy usually being formed in two or three minutes. The contents of the scorifier are then poured into a round bottom mould, allowed to cool for a few moments, and the cadmium button separated from the cyanide, which may be used a second and a third time before being discarded. The button is cleansed with hot water, placed in an ordinary humid assay bottle, and boiled in two ounces of 32° nitric acid. When the brownish red fumes have entirely disappeared, the solution is diluted with 100 cc. of distilled water and 5 cc. of a saturated solution of iron alum added as an indicator. The contents of the bottle are then titrated with a solution of ammonium sulfocyanate, 1 cc. of which is equivalent to 10 gold weight of silver. The complete precipitation of the silver is, of course, indicated by the formation of a brownish red color which will not disappear on shaking. The fineness of the sample is obtained by multiplying the direct burette reading by ten."

If this method be satisfactory for silver in mass melts, which are confessedly difficult to handle by cupellation, it ought to be even better for the general run of deposits in a vast majority of cases. Having already examined the cupellation method carefully, we have a good basis for comparing the results by the sulfocyanate method with cupellation results, and in making this comparison we shall get many more comparative determinations by cupellation in various laboratories.

In order to try out the sulfocyanate method thoroughly, the Assayer at the San Francisco mint prepared a series of 12 samples in duplicate, representing characteristic bullions which he thought would be suitable for the process. He made duplicate determinations of silver in each sample by both cupellation and the sulfocyanate method and forwarded the samples to the Bureau with his results. The samples were then distributed to various other laboratories in the Service and the same four determinations were made

TABLE XI—COMPARATIVE SILVER DETERMINATIONS (FINENESS) BY CUPELLATION AND SULFOCYANATE METHODS

	Cupel	No. 1	S-C	Cupel	No. 2	S-C	Cupel	No. 3	S-C	Cupel	No. 4	S-C
Original	201	198	219	5	19.5	254.5	350	5	275	275	277	277
Lab. I	202	197	219.5	5	19.5	255.5	249.25	5	275	275	275	275
Lab. I	203	179	223	220	255	239	278	272	272	272	272	272
Lab. II	203	178	220	220	256	244	279	272	272	272	272	272
Lab. II	204	175	221	223	253	248	254.25	5	278	275	277.25	277.25
Lab. II	205	25	192	225	225	253	256.75	5	254.75	278	277.25	277.25
Lab. III	201	178	226	220	253	243	278	273	273	273	273	273
Lab. III	197	174	224	224	253	242	277	276	276	276	276	276
Lab. IV	200	182	225	213	258	247	279	267	267	267	267	267
Lab. IV	201	180	227	226	257	245	279	275	275	275	275	275
Highest	205	25	198	227	256	254.75	279	277.25	277.25	277.25	277.25	277.25
Lowest	197	174	219.5	5	21.3	253	239	275	267	267	267	267
Range	8.25	20	7.5	13	5.5	15.75	4	10.25	10.25	10.25	10.25	10.25
SAMPLE B	204	198	221.5	5	220.5	257.5	250.5	5	275	274.5	274.5	274.5
Original	203	198	221.5	5	220.5	256.5	249.25	5	276	274.5	274.5	274.5
Lab. I	203	176	224	220	257	244	278	271	271	271	271	271
Lab. I	205	177	221	220	255	244	279	273	273	273	273	273
Lab. II	204	191.75	223.75	223.75	259.25	255	279	275	277.25	277.25	277.25	277.25
Lab. II	205	191.75	223.75	223.75	259.25	255	279	275	277.25	277.25	277.25	277.25
Lab. III	201	174	226	222	253	243	277	274	274	274	274	274
Lab. III	197	175(1/2)	224	223	252	245	276	277	277	277	277	277
Lab. IV	200	180	225	209	256.5	249.5	279	268	268	268	268	268
Lab. IV	205	180	225	227	257	247.25	279	275	275	275	275	275
Highest	205	198	226	227	259	255	279	277.75	277.75	277.75	277.75	277.75
Lowest	197	174	221.5	209	252.5	243	275	266	266	266	266	266
Range	8	24	4.5	18	6.75	12	4	11.75	11.75	11.75	11.75	11.75
SAMPLES A AND B	204	198	221.5	5	220.5	257.5	250.5	5	275	274.5	274.5	274.5
Original	205	25	198	227	227	259.25	255	279	277.75	277.75	277.75	277.75
Highest	205	25	198	227	227	259.25	255	279	277.75	277.75	277.75	277.75
Lowest	197	174	219.5	209	252.5	239	275	266	266	266	266	266
Range	8.25	24	7.5	18	6.75	16	4	11.75	11.75	11.75	11.75	11.75
SAMPLE A	302	299.75	329.5	326.25	348	344.75	377.5	375.25	375.25	375.25	375.25	375.25
Original	300	298	375	328.5	326.25	348	345.75	378.5	374.5	374.5	374.5	374.5
Lab. I	300	295	330	324	345	343	370	371	371	371	371	371
Lab. I	300	295	330	324	345	343	370	371	371	371	371	371
Lab. II	303.75	303.75	330.25	330.25	330	349.5	349.5	376.25	379.75	379.75	379.75	379.75
Lab. II	302.50	302.5	329.50	329.5	349.5	349.5	376.5	379.75	379.75	379.75	379.75	379.75
Lab. III	299	301	332	327	347	342	382	379	379	379	379	379
Lab. III	299	301	330	327	345	342	380	379	379	379	379	379
Lab. IV	306	291	332	321	348	342	380	362	362	362	362	362
Lab. IV	301	303	332	326	348	343	381	372	372	372	372	372
Highest	306	303	332	330	350	349	382	379.75	379.75	379.75	379.75	379.75
Lowest	299	291	328.5	322	345	342	369	362	362	362	362	362
Range	7	12	5	8	5	7	5	11	17	17	17	17
SAMPLE B	302	299.75	329.5	326.25	348	344.75	377.5	375.25	375.25	375.25	375.25	375.25
Original	301	297.5	328.5	326.25	348	344.75	377.5	375.25	375.25	375.25	375.25	375.25
Lab. I	300	295	330	322	345	343	379	371	371	371	371	371
Lab. I	302	298	331	324	346	345	378	372	372	372	372	372
Lab. II	304.75	303.75	329.25	331	350.25	350.75	376.75	378.75	378.75	378.75	378.75	378.75
Lab. II	303	303	331.5	325	350	350.5	375.75	379.75	379.75	379.75	379.75	379.75
Lab. III	303	301	328	327	349	342	376	376	376	376	376	376
Lab. III	304	302	329	327	345.5	338	372	376	376	376	376	376
Lab. IV	306	291	332	318	349	345	381	366	366	366	366	366
Lab. IV	303	303	333	321	348	349	383	381	381	381	381	381
Highest	306	305	332	330	350	350.5	383	378.75	378.75	378.75	378.75	378.75
Lowest	300	291	328	318	345	338	368	366	366	366	366	366
Range	6	14	4	12	5	12.75	15	12	15	15	15	15
SAMPLES A AND B	306	305	332	330	350	350.5	383	379.75	379.75	379.75	379.75	379.75
Original	299	291	328	318	345	338	368	362	362	362	362	362
Highest	306	305	332	330	350	350.5	383	379.75	379.75	379.75	379.75	379.75
Lowest	299	291	328	318	345	338	368	362	362	362	362	362
Range	6	14	4	12	5	12.75	15	12	15	15	15	15
SAMPLE A	302	299.75	329.5	326.25	348	344.75	377.5	375.25	375.25	375.25	375.25	375.25
Original	306	305	332	330	350	350.5	383	379.75	379.75	379.75	379.75	379.75
Lab. I	301	297.5	328.5	326.25	348	344.75	377.5	375.25	375.25	375.25	375.25	375.25
Lab. I	300	295	330	322	345	343	379	371	371	371	371	371
Lab. II	304.75	303.75	329.25	331	350.25	350.75	376.75	378.75	378.75	378.75	378.75	378.75
Lab. II	303	303	331.5	325	350	350.5	375.75	379.75	379.75	379.75	379.75	379.75
Lab. III	303	301	328	327	349	342	376	376	376	376	376	376
Lab. III	304	302	329	327	345.5	338	372	376	376	376	376	376
Lab. IV	306	291	332	318	349	345	381	366	366	366	366	366
Lab. IV	303	303	333	321	348	349	383	381	381	381	381	381
Highest	306	305	332	330	350	350.5	383	378.75	378.75	378.75	378.75	378.75
Lowest	300	291	328	318	345	338	368	366	366	366	366	366
Range	6	14	4	12	5	12.75	15	12	15	15	15	15
SAMPLES A AND B	306	305	332	330	350	350.5	383	379.75	379.75	379.75	379.75	379.75
Original	302	299.75	329.5	326.25	348	344.75	377.5	375.25	375.25	375.25	375.25	375.25
Lab. I	301	297.5	328.5	326.25	348	344.75	377.5	375.25	375.25	375.25	375.25	375.25
Lab. I	300	295	330	322	345	343	379	371	371	371	371	371
Lab. II	304.75	303.75	329.25	331	350.25	350.75	376.75	378.75	378.75	378.75	378.75	378.75
Lab. II	303	303	331.5	325	350	350.5	375.75	379.75	379.75	379.75	379.75	379.75
Lab. III	303	301	328	327	349	342	376	376	376	376	376	376
Lab. III	304	302	329	327	345.5	338	372	376	376	376	376	376
Lab. IV	306	291	332	318	349	345	381	366	366	366	366	366
Lab. IV	303	303	333	321	348	349	383	381	381	381	381	381
Highest	306	305	332	330	350	350.5	383	378.75	378.75	378.75	378.75	378.75
Lowest	300	291	328	318	345	338	368	366	366	366	366	366
Range	6	14	4	12	5	12.75	15	12	15	15	15	15
SAMPLES A AND B	306	305	332	330	350	350.5	383	379.75	379.75	379.75	379.75	379.75
Original	302	299.75	329.5	326.25	348	344.75	377.5	375.25	375.25	375.25	375.25	375.25
Lab. I	301	297.5	328.5	326.25	348	344.75	377.5	375.25	375.25	375.25	375.25	375.25
Lab. I	300	295	330	322	345	343	379	371	371	371	371	371
Lab. II	304.75	303.75	329.25	331	350.25	350.75	376.75	378.75	378.75	378.75	378.75	378.75
Lab. II	303	303	331.5	325	350	350.5	375.75	379.75	379.75	379.75	379.75	379.75
Lab. III	303	301	328	327	349	342	376	376	376	376	376	376
Lab. III	304	302	329	327	345.5	338	372	376	376	376	376	376
Lab. IV	306	291	332	318	349	345	381	366	366	366	366	366
Lab. IV	303	303	333	321	348	349	383	381	381	381	381	381
Highest	306	305	332	330	350	350.5	383	378.75	378.75	378.75	378.75	378.75
Lowest	300	291	328	318	345	338	368	366	366	366	366	366
Range	6	14	4	12	5	12.75	15	12	15	15	15	15
SAMPLES A AND B	306	305	332	330	350	350.5	383	379.75	379.75	379.75	379.75	379.75
Original	302	299.75	329.5	326.25	348	344.75	377.5	375.25	375.25	375.25	375.25	375.25
Lab. I	301	297.5	328.5	326.25	348	344.75	377.5	375.25	375.25	375.25	375.25	375.25
Lab. I	300	295	330	322	345	343	379	371	371	371	371	371
Lab. II	304.75	303.75	329.25	331	350.25	350.75	376.75	378.7				



laboratories beyond the description of the process printed in the annual report. It was a part of the object of the investigation to determine if this description was sufficient, and if the process was simple and accurate enough to yield satisfactory results in the hands of the general run of assayers without more rigid specifications as to the details of operating the method. Some of the operators, however, had had more or less previous experience with the method.

All the results reported are given in Table XI. The laboratory numbers do not always mean the same laboratory but the A and B samples were always assayed in the same laboratory. The figures given are finenesses, or parts per 1000.

An inspection of this table shows that some of the results were evidently vitiated by unusual accidents which were not appreciated at the time of making the determination. When the reports were received

Most of the figures given in various following tables are finenesses or parts per 1000.

Four of the samples were returned to the San Francisco Mint without informing them what they were and the following table compares the original results with the second reports:

Sample	No. 1				No. 2			
	Cupel	A	S-C	Cupel	B	S-C	Cupel	B
1st report...	254.5	250.4	257.5	250.4	201.0	198.0	204.0	198.0
	3.5	49.3	6.5	49.3	2.0	16.9	3.0	8.0
2nd report...	256.0	253.5	258.0	254.6	206.0	195.6	205.0	197.8
	8.0	5.5	7.0	.6	6.0	6.7	5.0	6.7
Gold....		654.5				632		

Results on the reassays by the San Francisco Mint of two other samples in this set are given beyond.

A sample of cyanide bullion from another office was assayed twice at the San Francisco Mint and once at another mint. The results are given beyond.

Two samples from each one of three bullions taken at a purchasing office were assayed in duplicate by both methods in the San Francisco Mint and at another mint with the following results:

Sample	No. 1		No. 2		No. 3	
	Cupel	S-C	Cupel	S-C	Cupel	S-C
Sample A	539.5	536.1	423.75	423.6	345.5	337.4
San Francisco mint.....	41.5	1	25	6	3.5	5
2nd mint.....	537.0	532.0	422.0	421.0	336.0	338.0
	6.0	1.0	1.0	1.0	8.0	8.0
Sample B	539.5	534.0	423.25	423.6	344.5	338.5
San Francisco mint.....	40.25	5.0	3.0	2.6	7.25	7.4
2nd mint.....	537.0	532.0	424.0	421.0	338.0	338.0
	6.0		3.0		6.0	4.0
Gold.....		303.5		265		215

Two samples each from two cyanide bars were compared in the same way, but in the second comparison the second mint was not the same as in the first.

Sample	No. 1		No. 2	
	Cupel	S-C	Cupel	S-C
Sample A	462	457	438.5	433.1
San Francisco mint.....	57	7	41.5	
2nd mint.....	459	454	442.0	434.6
	6.0		2.0	5.6
Sample B	455	455	433.5	430.8
San Francisco.....	3	1	5.25	2.0
2nd mint.....	451	445	438.0	434.6
	4	5	5.0	6.6
Gold.....		441		413

When the investigation of the San Francisco samples was inaugurated it developed that one of the small offices was already in the habit of using sulfocyanate titration on some deposits, and the following table shows their results on 15 bullions of widely varying composition arranged by progressively increasing silver fineness:

No.	No. 10		No. 11		No. 12		No. 13		No. 14		No. 15	
	Cupel	S-C	Cupel	S-C	Cupel	S-C	Cupel	S-C	Cupel	S-C	Cupel	S-C
390	390	396	393	530.5	527	531.25	529	532.25	530			
391	390	396.5	394	532.5	529	532.25	530					
392	390	397	394	532.5	529	532.25	533.25					
393	391	397	396	532.5	530	533	534.25					
394	391	397	398	533.5	530	534	534.25					
395	391	397.5	399	533.5	531	534	535					
395	391	398	399	534	531.5	534.25	536.5					
395	394	399	400	534.5	531.5	535.25	537					
395.75	395	399	401	537	531.5	535.75	537.5					
396	395	399	402	537	532	536	537.5					
396.5	397	400	402	537	532	536	537.5					
396.5	399	401	402	537.5	532	536.75	538					
397	401	401.5	402	538	534	538						
399	401.5	402	403	538.5	534.5	538.5						
399.5	401.5	402	403	538.5	535	539						
401	402	402		539.25		540						
401	402	403		539.25		540						
401.5				539.5		542						
403				539.5		542						
403				539.5		542						
406												
Range	13.0	12.0	10.0	10.0	9.0	8.0	10.75	9.0				

at the Bureau it was too late to investigate these erratic results. If now we discard these accidental results and group the remaining reports in regular numerical order we have the above table.

Nos. 1 and 4 were cyanide bars, No. 5 was a jewelry scrap bar and No. 3 carried lead as the main base metal. The original office numbers on these bars were between 85 and 115, mass-melts 3, 4, 5 and 6, and chips bar No. 4.

At the redeposit office five of these bars were also examined by the sulfoeyanate method, being original bar No. 95 and mass-melts 3, 4, 5 and 6.

Test	1st	2nd	3rd	4th
No. 95	12.1	13.2	12.2	12.2
	10.1	4.0	13.2	13.2
Mass 3	271.9	270.2	272.8	270.8
	.9	69.2	1.8	1.8
Mass 4	235.5	232.6	231.0	238.2
		4.7		9.2
Mass 5	186.5	181.8	187.3	186.3
	.0	7.0	6.3	4.2
Mass 6	256.7	258.0	258.5	258.5
		8.0	.5	.5

Different samples of the same bullion were submitted to three laboratories and assayed in duplicate by both methods. Ten of the 12 results fell between 441 and 444 fine in silver, showing a most remarkable agreement. Unfortunately, however, the other two results were much lower. The following are the detailed reports:

Laboratory	Cupel	Sulfoeyanate
1st.....	443.0	434.0
		5.0
2nd.....	444.0	441.9
	1.0	.9
3rd.....	441.0	444.0
	2.0	3.0
Gold.....		263.25

A very low bullion, 110 fine in gold, previously mentioned, carrying a very large amount of lead was cupelled 16 times and the silver determined by the sulfoeyanate method 13 times in various laboratories with the following results:

Fineness	Assays		Fineness	Assays	
	Cupel	S. C.		Cupel	S. C.
49.0	2	3	3.0	1	1
50.0	1	3	4.0	3	3
.5	1		8.0	1	1
.8	2		9.0	1	1
1.0	1	3	60.0	1	1
.5	1		1.0	1	1
2.0	1				
.25	1				
.5	3		16	13	

TABLE XIII. CYANIDE BULLION LOW IN SILVER

	No. 1		No. 2		G. L.	No. 3		G. L.
	Cupel	Sulfoeyanate	Cupel	S. C.		Cupel	S. C.	
Purchasing office.....	19.0	18.1	14.0	14.8		16.0	17.0	
	19.0	18.1	14.0	14.8		16.0	17.0	
1st laboratory.....	17.0	17.2	10.0	12.0	15.0	20.0	15.0	15
	14.0	16.8	17.0	12.0	14.5	19.0	15.2	16
2nd laboratory.....	19.25	18.6	15	12.25	13.0	16.5	15.4	14
	18.25	17.4	15	12.5	14.0	17.0	.6	14
3rd laboratory.....	20.0	16.9	18	15.5	11.9	14.0	15.9	16
	21.0	16.9	19	14.5	12.9	15.0	15.9	18
Gold.....		920.5		916.5			884.5	

Many other comparisons between these two methods are shown in the larger comparisons given beyond.

Once having the silver in solution, the Gay-Lussac method of titration with chloride of sodium should be an excellent method of determining the silver. To get satisfactory results, however, in a reasonable length of time, requires especial equipment, and it is essential to have a suitable shaking apparatus to settle the silver chloride precipitate. I have already described the

an approximation of the amount of silver in the bullion, such an approximation for instance as is supplied by the customary preliminary assay of gold bullion, in order to have the amount in a test a trifle over a gram. The required quantity of silver may be made up by taking the proper amount of the bullion for the assay, or sufficient pure silver may be added to give the required amount with that present in the bullion. This extra silver may be added before alloying with cadmium or it may be added to the final solution. If the silver is not adjusted and it is attempted to titrate an unknown amount from a burette, the operation becomes troublesome and less accurate. Our small offices are not equipped for the Gay-Lussac method and before going to the expense of equipping them it is essential to know if the method is sufficiently better than the sulfoeyanate method.

A sample of cyanide bullion, very low in silver, was tested in four laboratories with the following results:

CYANIDE BULLION VERY LOW IN SILVER: GOLD, 884			
Laboratory	Cupel	Sulfoeyanate	Gay-Lussac
1st.....	6.0	5.0	
	6.0	6.0	
	6.0	5.9	
2nd.....	6.0	5.0	5.5
	6.5	6.0	
	7.0		
3rd.....	6.0	5.0	5.5
	6.0	7.0	5.5
4th.....	8.0	7.0	6.5
	9.0	7.0	6.5
	9.0	7.0	8.0
	9.0	7.0	8.5

Three samples of bullion from the same mill as the last sample, a little higher in silver, were examined at the purchasing office by both cupellation and the sulfoeyanate method and then tested at three other laboratories by both these methods, and also by the Gay-Lussac method, with the results shown in Table XIII.

Top and bottom samples of a different cyanide

	TOP		G. L.	BOTTOM		G. L.
	Cupel	S. C.		Cupel	S. C.	
1st laboratory.....	59	59	59	58	55	61.0
	2	9	60	8	6	1.0
2nd laboratory.....	61	64	64	61	64	62.5
	3	6	6	0	2	6.0
Gold.....	57			57		

bullion were examined in two laboratories by the three methods with the above results.

	No. 1		No. 2		No. 3		No. 4		No. 5		No. 6	
	Cupel	S. C.	Cupel	S. C.	Cupel	S. C.	Cupel	S. C.	Cupel	S. C.	Cupel	S. C.
Purchasing office.....	238	256	277.0	277.0	350.0	409.0	439.0	439.0	439.0	439.0	439.0	439.0
1st Lab.....	234	228	253	229	346.0	349.0	410.0	405.0	410.0	437.0	433.0	440.0
	29	30	2	2	8.0	8.0	9.0	7.0	0	5.0	3.0	1.25
	36	27	2	1								
	9	0	3	3								
2nd Lab.....	230	230	280.0	278	349.0	352.1	410.0	410.0	410.0	440.0	441.0	441.5
	29	29	1	1	50.0	3	49.5	2.5	2.5	37.0	39.0	.0
3rd Lab.....	284	278	351.75	352.1	415.5	414.6	440.75	440.75	440.75	441.6	441.6	
	4	4	3.75	1	6.5	3.5	1.75	1.75	1.75	2.8	2.8	
Gold.....	525	529.25	173	240	511.5	511.5	258					

use of this method in our Mint Service.<sup>1</sup> In order to follow the mint practice closely it is essential to have

Most of the results in the above table were obtained in settling disputes and in some cases different laboratories worked on different samples. The purchasing office is the same in each case.

<sup>1</sup>"The Gay-Lussac Method of Silver Determination," THIS JOURNAL, 5, 209; Trans. A. I. M. E., 45, 256.

Sample No. 3 contained a great deal of lead.

Three of the original San Francisco samples were tested by the Gay-Lussac method in laboratory No. 3 as follows:

	Cupel	No. 2 S-C G.-L.	No. 4 Cupel S-C	G.-L.	No. 6 Cupel S-C	G.-L.
A.....	226	220 224.0	278 273	277.0	332 327	331
B.....	226	222 225.3	277 274	278.0	328 327	331
Gold.....	4	754.25	3	717	3	636.5

Two of the original San Francisco samples were returned to that institution without informing them what the samples were and the cupel and sulfocyanate determinations were repeated and Gay-Lussac determinations added as follows:

Assays	Cupel	No. 3 S-C G.-L.	No. 1 Cupel S-C	G.-L.
A1st.....	254.5	250.4	201	198.0
2nd.....	5.5	49.3	2	6.9
B 1st.....	256.0	253.5	206	195.6
2nd.....	8.0	5.0	6	6.7
Gold.....	257.5	250.4	204	198.0
	6.5	49.3	3	8.0
	258.0	254.6	250	197.8
	7.0	6.0	5	6.7
Gold.....	634.5		632	

Top and bottom samples of a cyanide bullion from a small office were sent to the San Francisco Mint twice without informing them what the samples were. The samples were sent to another mint without information as to the San Francisco results. The results reported were as follows:

	Top Cupel	S-C	G.-L.	Bottom Cupel	S-C	G.-L.
San Francisco Mint, 1st.....	140.5	136.7	...	142.9	135.5	...
2nd.....	4.5	7	...	3.9	1.0	...
2nd mint	147.0	139.9	139	145.0	141.0	138.0
Gold.....	39.0	41.0	8	41.0	2.0	7.0
	142.5	139.2	133	146.0	136.7	133.0
	3.5	8.2	4	3.0	.2	3.0
Gold.....	645					

Top and bottom samples of two cyanide bullions from the same office as the last were sent to the San Francisco Mint and the same second mint. The results reported were as follows:

	Top Cupel	No. 1 S-C	G.-L.	Bottom Cupel	No. 2 S-C	G.-L.
San Francisco.....	417.25	414.7	...	485.5	481.4	...
2nd mint.....	21.25	5.9	...	7.5	.4	...
Gold.....	420.5	417.7	420	486.5	483.8	489.0
	19.5	8.7	...	.5	6.3	91.0
Bottom San Francisco.....	416.0	415.9	...	485.75	480.2	...
2nd mint.....	21.0	.9	...	7.75	.1	...
Gold.....	419.5	418	422	487.5	483.3	489.0
	.3	.7	4	8.5	4.3	9.0
Gold.....	434			434		

Top and bottom samples of two more cyanide bullions from the same office were sent to the San Francisco Mint and to another second mint and were also returned to the purchasing office. The results reported were as follows:

	Cupel	No. 1 S-C	G.-L.	Cupel	No. 2 S-C	G.-L.
Top San Francisco Mint.....	449.5	441.2	...	448.0	437.4	...
2nd mint.....	2.5	0.3	...	7.0	40.2	...
Purchasing office.....	449.0	436.0	446	445.0	433.0	442.0
Gold.....	2.0	6.0	6	3.0	3.0	3.0
	9.0	.5	...			
Bottom San Francisco.....	446.5	438.2	...	452.0	444.8	...
2nd mint.....	7.5	9.1	...	0.0	5.9	...
Purchasing office.....	445.0	441.2	...	441.5	437.4	...
Gold.....	38.0	.2	...	0.5	8.3	...
2nd mint.....	448.0	445.0	443	444.0	433.0	441.5
Gold.....	2.0	5.0	4	50.0	3.0	2.0
	9.0	.3	...			1.0
Purchasing office.....	449.0	445.6	...	444.5	436.2	...
Gold.....	9.0	8.2	...	5.0	8.8	...
	386			380		

When the gold in the bullion is sufficiently low to permit the direct solution of the other metals in nitric

acid with the retention of only traces of silver by the gold there does not appear to be any real advantage in employing the cadmium treatment, as is well shown by the following comparisons:

The very low-grade bullion high in lead previously mentioned was assayed in various laboratories eleven times by the cadmium sulfocyanate method and ten times by direct solution in nitric acid and titration with sulfocyanate as follows:

Silver fineness	Cadmium assays	Nitric acid assays
45.0.....	1	1
46.0.....	2	1
49.0.....	1	2
50.0.....	1	1
51.0.....	5	4
51.25.....	1	...
52.0.....	1	...
53.0.....	1	1
Gold.....	11	10

Two other samples also high in lead but very much higher in silver yielded the following results:

Silver fineness	No. 1 Assays Cadmium	Nitric acid	No. 2 Assays Silver fineness	Cadmium	Nitric acid
281.4.....	2	...	441.2	...	1
281.5.....	1	...	41.3	...	1
2.0.....	1	...	5.9	2	...
Gold.....	173	...	263.25	...	...

Two ordinary samples of bullion yielded the following comparisons:

Silver fineness	No. 1 Assays Cadmium	Nitric acid	No. 2 Assays Silver fineness	Cadmium	Nitric acid
333.....	1	...	352.3	...	1
6.....	2	...	3.9	1	...
7.....	1	...	4.4	1	...
8.....	1	...	...	...	...
41.....	1	...	...	...	...
4.....	1	...	...	...	...
5.....	1	...	...	...	...
Gold.....	215	...	240	...	...

As the amount of the samples, left after making the main comparisons, allowed, four of the San Francisco bullions were assayed by direct solution in nitric acid and titration with sulfocyanate, yielding the following comparisons:

Silver fineness	No. 1 Assays Cadmium	Nitric acid	No. 3 Assays Silver fineness	Cadmium	Nitric acid
375.....	1	...	401	2	1
6.....	2	...	3	1	1
7.....	2	...	4	1	...
8.....	2	...	5	4	1
80.....	3	...	7	...	1
Gold.....	163.5	...	10	169	...
Silver fineness	No. 2 Assays Cadmium	Nitric acid	No. 4 Assays Silver fineness	Cadmium	Nitric acid
394.....	2	...	533	1	...
6.....	1	...	7	2	...
7.....	2	...	8	1	...
8.....	1	...	9	...	1
401.....	1	...	40	...	4
3.....	1	...	5	...	1
Gold.....	164.5	...	147.75	...	...

Careful consideration of these comparisons shows that the sulfocyanate method is capable of yielding very satisfactory results in many instances, but the widely varying results so often shown suggest the desirability of more explicit instructions for carrying on the method and especially of pointing out probable and possible sources of error in the manipulations. Therefore, each assayer, whose work has been used in this paper, was asked to write a history of his experience with the method. Also during the course of the



tests various observations have been reported from time to time regarding the operation of the method. A study of this data has brought out the following points:

Various assayers prefer to make the cadmium alloy in a small porcelain crucible or annealing cup over a Bunsen burner or small blast lamp. This allows the direct transfer of the weighed sample to the crucible or cup before heating and the omission of the lead foil container for the sample if desired. Dusty samples, however, should be enclosed in lead foil. The alloying operation is then easily observed and is under better control. Where much work is to be done, a copper stand to hold several assays may be made and this may be warmed up on the lip of the muffle or even inside the muffle after it has cooled down from other work, before heating over the lamp. Much less cyanide is required than in alloying in a scorifier. One assayer uses only three grams of cadmium. This, however, raises the question of the amount of silver retained by the residual gold. This point calls for further investigation. Personally, I am also convinced that the very foundation of the work, the question of the formation of a proper alloy with the cadmium, requires investigation.

Much serious objection has been raised against alloying the samples with cadmium in a scorifier in the muffle, liability to crack after short use, liability of particles of sample to escape alloying with the cadmium, difficulty of observing the process, liability of overheating with sudden evolution of gas, particularly on adding the Cd, which may project small particles of the sample out of the fusion, especially in the early stages of the operation, liability of small beads becoming entangled in the cyanide, particularly on pouring, are urged against this operation. Its chief advantage in allowing the reuse of the cyanide is greatly reduced by the fact that a much smaller amount of cyanide will answer in other containers.

There is very general objection to pouring the fusion and it is preferred to cool the fusion in the crucible or cup, and to run water, warm if possible, directly into the cool crucible or cup to dissolve the cyanide. Where much work is done an arrangement of small faucets allows the solution of the cyanide from several fusions at one time. A wire gauze frame, with gauze cover, to hold several crucibles and a suitable rose-sprinkler make a very convenient dissolving arrangement.

Two assayers assert very positively that the disappearance of fumes does not give sufficient heating of the solution, but that the solution must be vigorously boiled after that. Care must, however, be exercised to avoid mechanical loss of solution in this boiling. It is, therefore, better to dissolve the alloy in a conical flask rather than in a regular silver bottle. The titrating must be done absolutely cold, and all the conditions as to titrating must be kept as uniform as possible. When the bullion contains only a little silver some operators prefer to add a known amount of silver to the solution before titrating.

When titrating a solution of pure silver, as in stand-

ardizing the solution, the end point may be sufficiently sharp, but, as it so often happens with volumetric methods in general when applied to miscellaneous materials, so this method presents its most serious difficulty in determining the end point in practical work. Also, as usual, the personal equation of the operator exerts its greatest influence at this point in the method. While it helps the work along to know approximately the amount of silver present, the careful operator is not obliged to make a preliminary assay for this purpose.

It has been suggested to determine the silver in the base metal assay beads by sulfocyanate titration and some promising preliminary results were reported, but consideration of the question of cupel absorption in the base metal assay precludes the expectation of satisfactory results by this proceeding, unless the result be corrected by carrying the assay proof beads through the same operations. Manifestly this would consume too much labor and be too lengthy. However, the following interesting set of results on identical samples of a bullion may be given:

Lab.		Cupel	Silver		S-C beads	Gold
			G.-L.	S-C		
1st	.....	309.0	301.0	297.0	293.0	430.2
		10.0	2.0	8.0	3.0	.5
		1.0	2.0	8.0	4.0	.6
		2.0	3.0	8.0	4.0	1.0
		309.0	300.0	303.9	294.9	430.0
2nd	.....	.5	2.0	9	5.2	.8
		11.25	3.5	4.1	.5	1.1
		2.0	3.5	7	6.9	.6
		303.0	302.5	304.0	302.5	430.8
		4.0	.5	4.0	5	.9
3rd	.....	4.0	.5	5.5	6.0	1.0
		5.5	.5	9.5	10.0	1.0
		6.5				1.0
		7.5				.2
		8.5				
4th	.....	9.5				
		308.9	307.6	302	300	431.1
		9.9	.6	3		.1
		.9		4		.1
				5		1

During the progress of the work various abnormal results reported were investigated more or less. Most of these may be set down as due to some unusual and at the time unobserved accident or to the lack of proper care in observing obvious necessary precautions. Once or twice I suspect the use of water containing chlorides. One case, however, was so peculiar that it was thoroughly investigated, up to the practical exhaustion of the samples. It is No. 1 in the set of 12 San Francisco samples.

Duplicate samples of this bullion were cupelled for silver, in five laboratories, 12 times each, with the following results:

	A	B
197.0	1	1
200.0	1	2
1.0	3	1
2.0	1	
3.0	2	2
4.0		2
4.5		1
5.0	2	3
6.0		
	12	12

The silver was also determined by the sulfocyanate method in the same five laboratories 12 times, and on each sample there is a group of corresponding high and low results, as follows:

	A	B
174	1	1
8	1	1
6	1	1
2	1	1
8	2	1
9	1	1
80	1	1
2	1	1
92	1	2
3	1	1
6	1	1
7	1	1
8	1	3
	12	12

One of the laboratories also determined the silver by the Gay-Lussac method at 196 and 7 for A, and 197 and 7 for B.

The preponderance of the evidence is strongly in favor of the high sulfocyanate figures, but the 12 low results obtained in three laboratories cannot be ignored, and it became most important to ascertain, if possible, the cause of these low results.

The balance of the samples was, therefore, sent to one of the laboratories with instructions to examine it most carefully, and especially to watch the sulfocyanate titrations for indications that might warrant stopping the titrations within the limits of the lower range of results already reported.

Curiously enough, however, this examination also developed serious difficulty with the Gay-Lussac titration. The following is the assayer's report upon his work.

"The samples of bullion transmitted in the letter of the Director of the Mint of the 15th, marked IIA and IIB, have been carefully assayed, partly by myself and partly under my close observation, with the results which are peculiar and surprising, as shown below.

"Two assays were made for gold, giving 632.5 and 632.9. By the three methods of determining silver the following results were obtained, proof corrections being made in each method:

	Cupel	Silver G. L.	Sulfocyanate
A	205 1/2	181	191
	204 1/2	184	191
		184	190
B		183 filtered	
	199 1/2	182 1/2	190
	206 1/2	182	188
	202	182	190 1/2
	200	184 filtered	

The cupellation results were first obtained and three assays from each sample were then made by the Gay-Lussac and three by the sulfocyanate.

"The appearance of the gold in the bottom of the containers, after dissolving two cadmium buttons in nitric acid 32° B., was unusual. The gold remained as a fine dark powder and long-continued boiling failed to lighten the color or cause it to become somewhat aggregated, which is quite unlike the usual character of such undissolved remainders.

"In working by the sulfocyanate method, as the silver was precipitated, the solution became of a dark bluish color, which made the end point difficult to determine. Quite consistent results were obtained, however, and the accuracy of the operator's judgment was checked by adding sulfocyanate to a much more decided end point three to five points higher, and then working back with silver solution to the disappearance of the color, closely confirming the original results.

"In working by the Gay-Lussac method, after addition of 100 cc. standard salt solution and agitating, the solution was somewhat dark, but not enough apparently to interfere with a fairly correct determination of the end point.

"Upon comparing results from the three methods, it was at once noted that the chloride had given the lowest results. A re-assay was, therefore, made upon each sample by that method, filtering to a clear solution to determine the end point.

"These two assays, shown above, varied but little from the original, one being a little lower and the other somewhat higher.

"It was then thought that the presence of palladium or some of the platinum metals might account for the high cupellation results, but upon trial no indication of such metals was obtained. On the assumption, then, that base metals might have formed compounds interfering with the humid determination, and to eliminate this factor, six new cupellations were then made of one-half gram each, two from the A sample and four from the B sample, there being more of the latter, and the silver content of the button determined. Corrected by corresponding proofs, these gave the following results:

	Cupel silver		Humid silver
A	203 1/2	Cl	204 1/2
A	202 1/2	S	203
B	201 1/2	Cl	204
B	197 1/2	S	204
B	204 1/2	Cl	205 1/2
B	203 1/2	S	205

"Each of these buttons, together with each of the proofs used, was fused with cadmium and the actual silver content determined, three by the chloride method and three by the sulfocyanate, giving, after making the proof corrections, the results shown in column headed 'Humid Silver.' Those worked by chloride are marked Cl, and the others by S.

"These results confirmed the high results obtained by cupellation and indicated the presence of silver in some form which failed of solution in the nitric acid. An assay of A and B was, therefore, made, fusing with cadmium and dissolving in nitric acid as usual. Sulfuric acid was then added and an additional long boiling given. These were then worked by the chloride method and showed silver 182, no better than the original determination by this method.

"Two grams of the sample were then fused with cadmium and parted in nitric acid with long-continued boiling. The residue was then filtered off, washed, dried, dissolved in *aqua regia*, nitric acid removed by evaporation, and, upon redissolving in hydrochloric acid and dilution, silver chloride showed in considerable amount. It was collected on filter, burned and cupelled, giving 40.5 mg. This button was dissolved in nitric acid titrated with sulfocyanate, and showed 39 mg. of silver, the remainder of the button being gold. From previous experience, 2 1/2 mg. was allowed for the loss in cupellation, making 41 1/2 mg. here found in the residue. The gold in the filtrate from the silver chloride was recovered and upon assay was found to contain 3 1/2 mg. of silver, making a total in the original residue of 45 mg.

"The filtrate from this residue containing the silver soluble in nitric acid was titrated with sulfocyanate and gave 364 mg., which, added to the 45 mg. previously recovered from the residue, gave 409 mg., equivalent to a fineness of 204 1/2 silver, which corroborates the higher of the cupellation returns.

"Apparently, the sulfocyanate, when titrated directly into the solution containing residue, has some effect upon the undissolved silver which sodium chloride solution has not, as the titration upon the filtered solution above, thoroughly washed, gave returns agreeing with those by the Gay-Lussac method, while those directly titrated had run 7 to 8 thousandths higher.

"The filtrate from the precipitated gold by qualitative analysis was found to show traces of mercury, copper, iron, arsenic and tin.

"The lack of more of the metal prevents any further investigation of the nature of the base metals contained, but the work above described seems to show that the variation in the results, and the low returns obtained by the humid processes, are due to the imperfect solution of this peculiar material in nitric acid."

It is, therefore, certain that this particular bullion is quite unsuited for the determination of the silver by either one of the volumetric methods.

In elucidating the operations of the method two institutions have made many tests upon synthetic preparations or proofs. For the most part these tests were made to determine the effect of copper upon the method, but various proportions of other metals and combinations were also tried.

In one institution 12 synthetic proofs were weighed up, fused with cadmium, and titrated with sulfocyanate with the following results:

Titration fineness	Parts per 1000 weighed up			
	Silver	Gold	Lead	Copper
247.3	250	750		
247.3				
248.9	250	500	250	
246.7				
248.9	250	250	500	...
248.9				
249.5	250	250	250	250
250.6				
250.6	250	...	500	250
251.7				
251.7	250	...	250	500
249.5				
249.5	250	...	250	250
250.6				
249.5	250	250	...	250
249.5				
247.3	250	250	250	...
251.7				
251.7	250	...	...	250
495.0				
495.0	500	500		
748.6				
748.6	750	250	...	...

In eight other cases the various metals were weighed into flasks, dissolved direct in  $\text{HNO}_3$ , and titrated with sulfocyanate. The following are the results obtained:

Titration fineness	Parts per 1000 weighed up			
	Silver	Lead	Copper	Zinc
249.9	250	...	500	250
249.9				
251.0	250	...	750	...
249.9				
249.9	250	...	250	500
247.7				
246.6	250	...	...	750
247.7				
249.9	250	250	250	250
250.4				
248.8	250	500	250	...
247.7				
248.8	250	500	...	250
249.9				
248.8	250	750	...	...

These results show a general tendency to get higher results in the presence of copper.

In the second laboratory 10 cadmium fusion tests on synthetics yielded the following results:

Titration fineness	Parts per 1000 weighed up					
	1	2	3	4	5	6
49	48	48	48.0	49.0	...	48.4
49	50	50	50.0	53.0	...	50.3
51	50	50	51.5	50.5	...	50.7
53	51	52	52.0	52.0	...	52.0
149	151	152	150.0	149.0	...	150.0
152	152	153	152.0	152.0	...	151
152	151	152	152.0	152.0	...	152.0
154	154	153	153.0	154.0	...	154.0
451	449	450	451.0	449.0	...	450.0
452	453	452	452.0	452.0	...	452.0

Five duplicate tests yielded the following results:

Titration fineness	Parts per 1000 weighed up		
	Silver	Gold	Copper
77	75	850	75
75.5			
101	100	800	100
2			
103	100	600	300
53			
53	50	650	300
80			
79	75	550	375

These tests still more clearly indicate a tendency to high results in the pressure of copper.

The following tests were obtained by direct solution of the metals in nitric acid:

Silver found	Metal taken		Silver found	Metal taken	
	Silver	Copper		Silver	Copper
15	15	...	26	25	300
199	200	...	252	250	300
80	80	100	102	100	500
301	300	100	502	500	500
51	50	200	...	...	...
202	200	200	...	...	...

A set of six tests in duplicate on synthetic proofs alloyed with cadmium yielded most interesting and surprising results as follows:

Silver found	Metals taken		
	Silver	Gold	Copper
10	10	900	100
9			
27	30	800	200
54			
48	50	700	300
104			
100	100	500	400
207			
199	200	300	500
406			
397	400	...	600

It will be noted that in every instance one result in each set is much lower comparatively than the other and in five cases the lower result is below the amount of silver taken, notwithstanding the pressure of so much copper.

It is, therefore, apparent that at times some other influence may overbalance the tendency of copper to give high results. Manifestly this is the visual condition of the operator. Some eyes are always better than others in distinguishing shades of color, but even the best of eyes have their off days.

The net result of this work on synthetics is that if accurate results are desired proofs must be run with the assays. Proofs will not only correct for the composition of the metal but also for the visual variation of the operator. Of course, in miscellaneous work the bullions may be grouped and a generalized proof used for several titrations, just as such a general proof is often used in cupellation work.

In the course of some previous work, in the second laboratory, mentioned above, in testing the Gay-Lussac method on cadmium fusions, it was thought that the cadmium alone had a slight tendency to increase the silver figure, estimated at one one-thousandth. The results, however, were not entirely conclusive. If there be such a tendency then it is all the more necessary to run proofs in the sulfocyanate titrations for accurate work.

The following is a final general and practical illustration of the whole subject: During the time that the active investigation of the sulfocyanate method was in progress a small office shipped 11 bars weighing 11718.60 ozs. to a mint. On this shipment the mint reported 25.59 ozs. of silver in excess of the assay office report. Most of the difference between the two institutions occurred in five bars weighing 3155.75 ozs.

The assay office top and bottom samples of these five bars were forwarded to the Bureau and the silver was determined by cupellation. The samples were also sent to two disinterested mints and the silver



TABLE XIV

	No. 1			No. 2			No. 3			No. 4			Nitric acid			No. 5			Nitric acid		
Top	Cupel	S. C.	G. L.	Cupel	S. C.	G. L.	Cupel	S. C.	G. L.	Cupel	S. C.	G. L.	Cupel	S. C.	G. L.	Cupel	S. C.	G. L.	Cupel	S. C.	G. L.
Purchasing office	161.75			490.0			467.0			660.0						668.75					
	2.0			25			7.0									7.5					
Bureau	160.50			403.0			471.75			666.0						673.5					
	7.5			25			2.0			7.5						4.25					
1st mint	161.75	161.6		399.75	404.2		470.75	471.6		665.0	667		665.9			673.25	672.6		673.8		
	7.5	2.7		401.75	401.2		471.75	470.6		8.0			7.0			4.25	3.8		8		
2nd mint	158.0	159.0	162	402.0	401.0	403	468.0	469.0	473	661.0	662	663	664			664.0	667.0	671	670.0		
	160.0	161.0		4.0	1.0		71.0	9.0		5.0						9.0	7.0				
	4.0			6.0			3.0			6.0						70.0					
Bottom																					
Purchasing office	160.0			400.25			465.5			658.5						667.50					
	25			1.25			3			7.5						2.5					
Bureau	161.0			403.50			470.75			667.25						673.0					
	1.0			7.5			1.0			5.0						2.5					
1st mint	160.75	161.6		400.75	402.0		471.25	470.5		667.0	665.9		667			673.25	672.6		672.6		
	1.75	2.7		1.75	3.1		2.75	5		8.0	9		7			3.25	6		3.8		
2nd mint	156.0	159.0		402.0	400.0		470.0	468.0		665.0	661.0		660			671.0	666.0		671.0		
	164.0	161.0		4.0	2.0		1.0	9.0		5.0	2.0					5.0	670.0				
Gold				742.25			560.25	486.25			245					242.75					

determined by cupellation and by the cadmium sulfo-cyanate method. On two samples the silver was determined by direct solution in nitric acid and sulfo-cyanate titration. Also a few cadmium Gay-Lussac determinations were made. Table XIV summarizes these determinations:

#### GENERAL CONCLUSIONS

While in the vast majority of cases cupellation yields fairly concordant results, yet the determination of silver by this method in different laboratories often shows a difference of 5 in the fineness reported. Occasionally much larger differences are shown. In the comparisons, differences of 5 fine between individual determinations in the group are common. Even duplicate assays often show a difference of 5 fine.

While in the cadmium sulfo-cyanate determinations wide differences often appear, yet in many cases the results agree among themselves and are often fully as concordant as the corresponding cupel results. Many of the differences are undoubtedly due to lack of familiarity by the operators with the method. The method has not been extensively employed and is comparatively new, when considered in connection with the many years of wide application of the cupellation method. With more extended and extensive use much better agreement in the results could be expected. On the whole, therefore, this paper shows that the sulfo-cyanate method compares favorably with cupellation and stands a good chance of supplanting the older method in large permanent laboratories where accuracy is desired.

Notwithstanding the unfavorable opinion of my predecessor, Dr. Whitehead, this work on cadmium fusions has impressed me favorably towards this operation as a promising method for determining gold in bullion and I am now sending out samples to test this fusion for that purpose.

LABORATORY, BUREAU OF THE MINT  
WASHINGTON, D. C.

#### THE EFFECT OF BREAD WRAPPING ON THE CHEMICAL COMPOSITION OF THE LOAF

By H. E. BARNARD AND H. E. BISHOP

Received June 20, 1914

With the passage of sanitary food legislation and the appreciation by both manufacturers and consumers that the production of clean food is even more important than the prevention of sophisticated food,

has arisen the demand for the protection of bread and bakery products between the oven and the home. Those who are familiar with the facts admit, without question, that the loaf as it leaves the oven is practically sterile both in the interior of the loaf and on the surface.

In the process of baking, the interior of a loaf of bread is raised to nearly 100° C. and at the same time is filled with moist steam, while the outside is subjected to a temperature of about 200° C. Under such conditions yeast cannot live. Most bacteria will not resist prolonged steam heat and all bacteria on the outside of the loaf are unquestionably<sup>1</sup> destroyed.

Roussel<sup>2</sup> has observed that during baking the temperature of the interior of the loaf reaches 101–103° C., and that of the crust 125–140.5° C. This temperature is somewhat higher than that reported by Mallett,<sup>3</sup> who found that the interior of the loaf did not get higher than 100° C. and usually ran lower, even as low as 92° C. Likewise in a series of determinations of the temperature of the interior of the loaf reported in the *Journal de Pharmacie et de Chimie*<sup>4</sup> it is shown that the temperature of the interior of the loaf as it leaves the oven is between 97° and 100° even after the baking has continued forty minutes. These temperatures are deemed sufficiently high to kill pathogenic bacteria but not as a rule the spores, except in the crust.

Numerous authors have pointed out that unprotected bread acquires a bacterial flora frequently very extensive, both as to variety and number.

Sadtler, in his report on bread wrapping to the National Association of Master Bakers, shows that the colon bacillus was present on the surface of seventeen per cent of unwrapped bread samples examined and that in addition to this number twelve and a half per cent showed the presence of such large numbers of bacteria as to be classed as of doubtful quality. On the other hand, samples of wrapped bread showed relatively low bacterial counts and the presence of no pathogenic organisms.

In addition to the necessity for keeping bread in a condition suitable for food, it must be protected

<sup>1</sup> Golden, *Proc. Ind. Acad. Sci.*, **1892**, 46.

<sup>2</sup> Roussel, *Univ. Paris, Rev. Internat. mil.*, **20**, 122, 31.

<sup>3</sup> *Chemical News*, Nos. **1515**–**1516**.

<sup>4</sup> *Journal de Pharmacie et de Chimie*, Series 5, **27**, p. 16

from the development of so-called bread diseases caused by microorganisms, all of which, with the exception of rosey bread, are of exterior origin. The spores or bacteria get into fissures in the crust and grow from thence into the crumb where they may multiply with extraordinary rapidity. It is true that the ordinary bakers' bread is rarely subject to disease since it is consumed before moulds or bacteria have an opportunity to grow within the loaf.

The common green mould, *Penicillium glaucum*, the spores of which are ever present in the air, sometimes develops quickly on the crust of bread which is placed in damp and mouldy receptacles. As in the case of bacteria, the best precaution against mould fungi is to place the bread at once on removing it from the oven in a cool, dry and airy place and keep it there.<sup>1</sup>

Because of the desire of the consumer for fresh bread, that is, bread having a peculiar quality of flavor and texture observed in bread recently drawn from the oven, bakers follow the practice of returning to the shop all bread left unsold at the end of a period varying from one to two days. Such bread is called second day bread and is described as stale or half stale although as a matter of fact, it is still entirely palatable and nutritious.

When bread is returned to the bakeshop it loses its value for human food and is finally disposed of as stock food, or in some instances, it is in part converted by suitable methods into sugars which are incorporated in the doughs for other bakings.

The loss to the baker occasioned by the return of loaves is so great that a study of the reasons producing staleness or half staleness, and methods by which this condition may be avoided is of importance.

Katz<sup>2</sup> has studied the change resulting in staleness, and has reached the conclusion that there exists within the crumb of bread a physico-chemical equilibrium; at a temperature between 50 and 100° C., normal fresh bread is the stable form, while at room temperature, 0 to 25° C., stale bread is the stable form. This observation is the more readily understood in the light of our present knowledge of colloidal chemistry, which has taught us that bread is a starch colloid, that is, that the starch granules composing the crumb are colloids which hold a considerable quantity of water in combination.

Birmbaum,<sup>3</sup> long before the development of the chemistry of colloids, called this condition "fixation" of the water. Fresh baked bread, as is shown in the accompanying charts, contains much more water in the interior than in the crust of the loaf. The interior crumb is in a perfect colloidal condition with a rather high moisture content, but as the bread grows old the ratio of the water content between crust and crumb is changed, the "fixation" water of the crumb leaving it to be absorbed by the relatively drier crust.

Boussingault<sup>4</sup> studied the distribution of moisture

and observed that by heating the crumb to 70° C., it became, in every respect, like fresh bread.

Bibra<sup>1</sup> confirmed Boussingault's observations but pointed out that when the water content falls below 30 per cent, heating does not suffice to remove the staleness. He observed that when the per cent of water falls below 30 per cent if the bread is immersed in water for a few seconds and then heated to about 80° C., it is then rendered fresh. Bibra, however, is inclined to regard the changes producing staleness as due to some change in the form in which the water is combined in the substance in the bread. Fresh bread, he suggests, contains water chiefly in the uncombined state, but on keeping, the moisture content gradually enters into chemical combination. As soon as this process is completed the bread is perfectly stale. Upon heating, however, the union of starch and gluten with the water is severed and the bread becomes fresh, provided sufficient water is present. This observation is of particular bearing on the practice of bread wrapping if it can be shown that the wrapped bread loses its moisture content more slowly than the bread which is not protected against evaporation.

Interesting as these theories are, the baker has not yet been able to utilize the suggestion that stale bread may be rejuvenated by heating, because of the fact that the restored freshness is lost rapidly and that bread so treated very shortly acquires its original staleness.

Other factors unquestionably enter into the development of staleness. It has always been noted that stale breads, especially rye and bran breads, develop an increasing acidity with age. The free acid invariably present in bread is for the most part a product of fermentative action in the dough. The acid reaction is caused by two factors, free organic acids and acid potassium phosphate. The latter acidity results from the action of the free organic acid on the neutral phosphates contained in the flour. The organic acids present in bread are in part volatile as acetic and butyric acids and in part non-volatile as lactic and some of the higher fatty acids. Occasionally an increase of acidity takes place during the storing of bread which becomes slimy in consequence of the growth of microorganisms, the spores of which survive the heat of the bake oven.

This microorganism, known as *Bacillus mesentericus vulgaris* (Flügge) or the potato bacillus, is most commonly met with in bread rich in bran and having a high water content. The abnormally high acidity produced by this bacillus is hardly ever met with in white bread. Stiegeler<sup>2</sup> quotes Lehmann to show that the volatile acids, chiefly acetic, constitute about two-thirds of the total acids contained in bread. Lehmann proposes the following qualification with reference to the acidity of bread:

100 GRAMS OF THE FRESH CRUMB REQUIRE	
1 to 2 cc. Normal alkali	Sweet loaf
2 to 4 cc. Normal alkali	Very slightly sour
4 to 7 cc. Normal alkali	Slightly sour
7 to 10 cc. Normal alkali	Fairly sour
10 to 15 cc. Normal alkali	Strongly acid
15 to 20 cc. Normal alkali	Excessively acid

<sup>1</sup> Stiegeler, "Pure Products," 3, 464.

<sup>2</sup> Zeit. für Elektrochem., 19, 206 and 663.

<sup>3</sup> Birmbaum's "Das Brotbacken Braunschweig," 1878, p. 255.

<sup>4</sup> Boussingault, Ann. chim. phys., [3] 36, 490

<sup>1</sup> D. Cereidarten uxdas Biot.

<sup>2</sup> Dr. H. Stiegeler, "Pure Products," 2, 183.

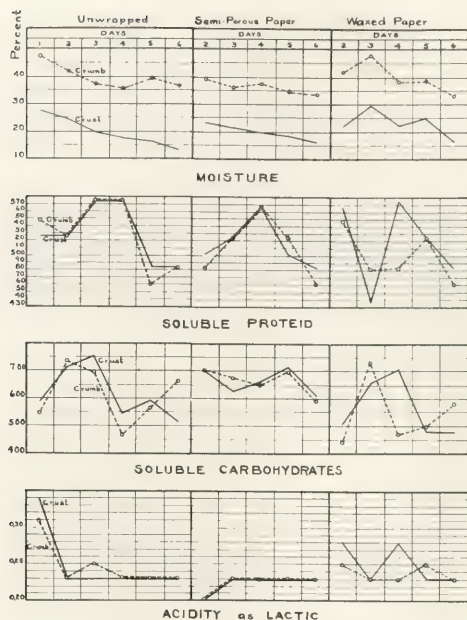


CHART 24—STRAIGHT DOUGH PAN BREAD

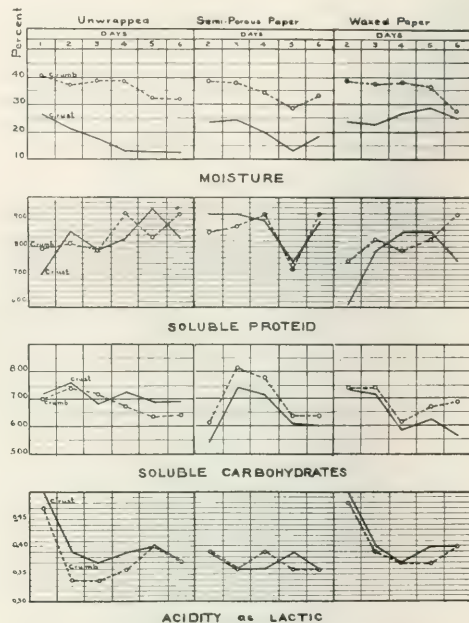


CHART 25—STRAIGHT DOUGH RYE BREAD

It is to the interest of the baker and of the consumer alike to protect bread properly until it is consumed. In recent years this has been attempted by the use of bread wrappers or paper prepared for the purpose in which the bread is wrapped before it leaves the bakery. The use of the bread wrapper has received general public approval and in some cities and states has been made the subject of legislation. Many bakers have found bread wrapping profitable both in the lessening of the loss due to stale bread and the increased approval of consumers, but on the other hand bakers have not viewed the adoption of the wrapper with favor, claiming that the use of the wrapper involves an additional cost for labor and wrapping material, the rearrangement of hours of labor at the bakery and further, that wrapped bread loses its flavor and becomes unpalatable more quickly than unwrapped bread. It is evident that if the wrapping of bread tends to injure the quality of the loaf the sanitary feature of the practice is not alone a sufficient argument for wrapping, since undoubtedly other methods of protection may be employed to prevent bacterial infection.

A number of investigations have been made of the effect of wrapping upon bread. The authors have studied the loss of moisture in the wrapped and unwrapped loaf and noted organoleptically the change in odor, flavor and acidity and the growth of moulds.<sup>1</sup>

They observed that the ordinary bakers' loaf wrapped in paraffined paper retained its good condition for three, four and, in some cases, five days, while the unwrapped loaf became dry at the end of two days.

<sup>1</sup> Barnard and Bishop, Indiana State Board of Health, *Rep.* 1910, p. 324.

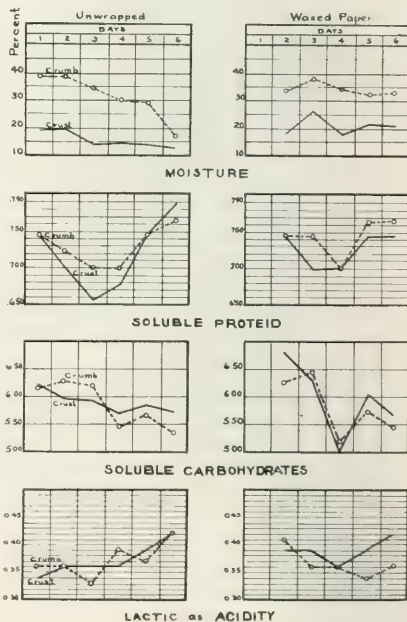


CHART 26—SPONGE DOUGH RYE BREAD



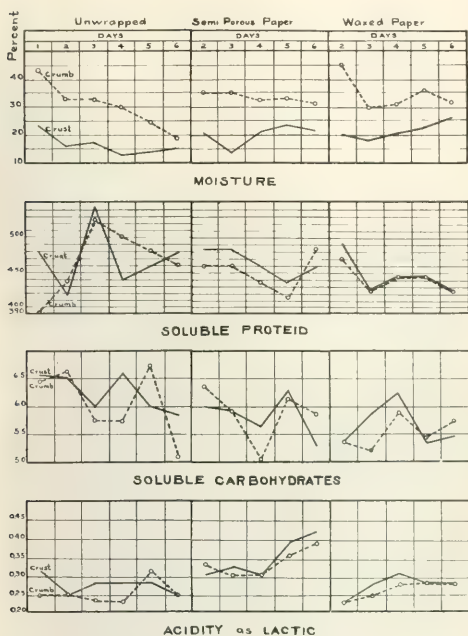


CHART 27—STRAIGHT DOUGH VIENNA HEARTH BREAD

The loaves in the porous paper wrapper dried out more rapidly than those wrapped in the paraffined paper but showed less tendency to sour. The wrapped Vienna and rye loaves lost their natural characteristics rapidly as the moisture in the center of the loaf became distributed throughout, thus injuring the flavor and texture of the crust which is considered the most desirable characteristic of such loaves.

Thomas<sup>1</sup> studied the practice of wrapping bread in paraffined paper noting the condition of the loaf 18, 36, 60 and 108 hours after baking. The paper used was of such grade that the loaf was practically sealed from the air. The authors note that the loaves wrapped hot lost less moisture than those wrapped cool, and that they kept as well and were in better flavor and aroma. The unwrapped loaf lost moisture rapidly together with flavor and aroma. Another series indicated that the effect of placing the unwrapped loaf in a clean unclosed compartment was much the same as wrapping. It is further noted that the wrapping did not prevent the loaf from becoming stale after 36 or 48 hours.<sup>2</sup>

In the same experiments, White determined the acidity of the same loaves. His results are summarized as follows: Bread made under cleanly conditions from a good quality of flour and yeast does not grow acid whether wrapped or not, even after 108 hours. Bread wrapped while warm and bread wrapped while hot show an increase in the acidity of the inside

<sup>1</sup> Special Bulletin Food Department, Gov. Agr. Expt. Sta., North Dakota, Vol. I, No. 26 (1910), 212.

<sup>2</sup> White, Special Bulletin Food Dept., Govt. Agric. Expt. Station, North Dakota, Vol. I, No. 26 (1910), p. 214.

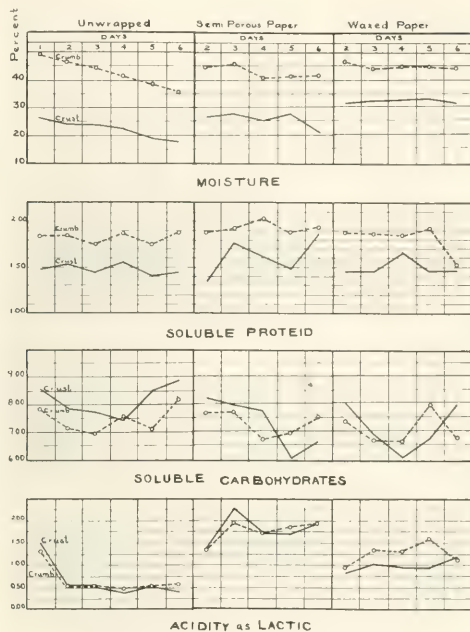


CHART 28—SPONGE DOUGH BOHEMIAN RYE BREAD

portion of the loaf as compared with the crust. This increase amounts to 9 per cent in the case of the hot wrapped bread.

The change of distribution of moisture is accompanied by the development of a different odor and flavor to which bakers have applied the phrase stale and half stale. When in such condition the modern taste is not so easily satisfied as with the fresh bread. Accompanying this change of moisture content are slight chemical changes in the composition of the bread, namely, in the proteids, sugars and acidity.

These facts have important bearing on the question of bread wrapping. It is claimed by bakers who object to the wrapping of bread<sup>1</sup> that when bread is kept in a close, warm, moist atmosphere from the time of baking or when new, it is far more likely to develop sourness and mould, than if stored where it may cool rapidly and lose any excess of moisture. The arresting of the passage of the moisture through the crust, and the concentration of the moisture in the crust is in every way injurious to the latter, and the arresting of the so-called normal loss of moisture will as well injuriously affect the interior of the loaf. They claim that milk bread and sour dough bread spoil more rapidly if the moisture is shut in and acidity develops.

These observations, which have become a positive expression of the belief of bakers adverse to wrapping, may, we believe, be proved or disproved by chemical means, and in an endeavor to arrive at the facts, we

<sup>1</sup> Sadler, Report 16th Convention National Association of Master Bakers, 1913.

have studied the composition of wrapped and unwrapped loaves kept under normal conditions for a period of days.

The bread was obtained from the bakeries within three or four hours after baking. By this time it had thoroughly cooled. During the preliminary work the different loaves were analyzed at once. When the study of the wrapped loaves began eleven loaves were taken for each set. Beginning on Monday, five loaves were wrapped and six were left unwrapped. One of the unwrapped loaves was analyzed on Monday. On Tuesday one unwrapped loaf and one wrapped loaf were examined. On Wednesday the second unwrapped and second wrapped loaf were analyzed. This procedure was followed through the week or until the whole set had been taken care of.

This plan gave us a series of loaves of bread that had

monly baked in this country. We have, therefore, felt it desirable to begin the work by establishing the standard composition of freshly baked bread. The following factors have been determined: moisture, ash, proteid, total solids, soluble solids, starch, soluble carbohydrates and acidity as lactic acid.

#### COMPOSITION OF BREADS STUDIED

The breads examined were obtained at the local bakeries and the samples were part of their daily baking. An effort was made to select loaves as uniformly baked as possible. Only the regular brands were analyzed, no effort being made to cover the whole field of bakery products.

The first loaves examined were of the straight dough variety, baked in single pans and of the following ingredients: cottolene, sugar, salt, yeast, flour, and water. The mixing and most of the handling were

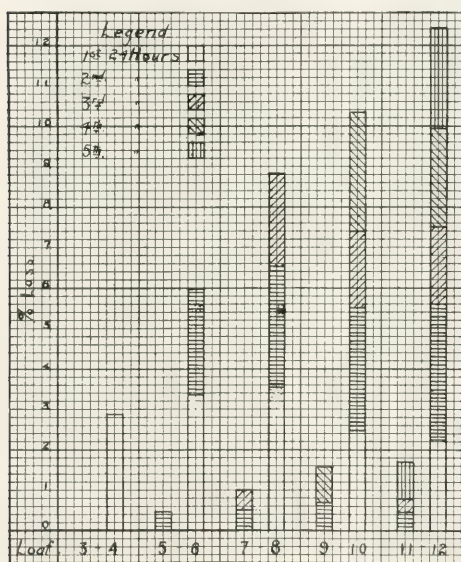


CHART 29—DAILY LOSS OF MOISTURE  
SET C—STRAIGHT DOUGH PAN BREAD

Odd numbered loaves wrapped in paraffin paper—Even numbered loaves unwrapped

been unwrapped 1, 2, 3, 4, 5, and 6 days each and a series of which had been wrapped 1, 2, 3, 4 and 5 days each.

Sets referred to as C, D, E, F, G and H were handled in this manner. For Sets I and J instead of analyzing a set of unwrapped loaves for every set of wrapped loaves we combined the series of wrapped loaves using 16 loaves instead of 11 loaves, six were left unwrapped, five wrapped in paraffin paper and five in a semiporous paper. This required the analysis of three loaves each day instead of two.

#### NORMAL COMPOSITION OF FRESH BREADS

The data at hand showing the normal composition of freshly baked bread is scanty. Most of the material available refers to foreign breads or breads not com-

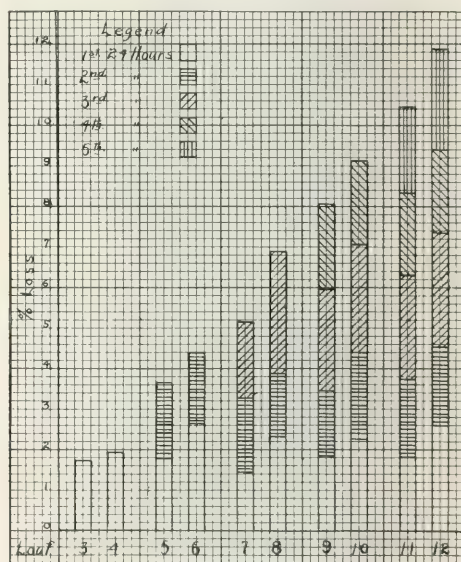


CHART 30—DAILY LOSS OF MOISTURE  
SET D—STRAIGHT DOUGH PAN BREAD

Odd numbered loaves wrapped in paraffin paper—Even numbered loaves unwrapped

done by machinery. The sponge dough hearth bread was made at the same bakery and contained salt, sugar, yeast, lard, flour and water.

In another set of experiments a somewhat different straight dough pan bread was used. This brand is baked as a double loaf. It is sold in a semiporous wrapper at ten cents. Its ingredients are the same as the loaves examined first but as a different formula is used the two breads are very different in flavor.

The straight dough pan bread was baked at another bakery. This sample contained malt extract, milk and cottonseed oil as well as the ordinary salt, sugar, yeast, flour and water.

The straight dough rye bread was made from a mixture of about 50 per cent rye flour and 50 per cent

wheat flour together with salt and yeast. This gave a loaf of very much the same texture as the ordinary white loaf.

The sponge dough rye bread was made from a rye flour mixture containing about 50 per cent rye. A portion of the dough from the day before was added, together with some fresh yeast to get the raising power. No shortening was used and salt only added to the mixture. The texture of the crumb was quite similar to the ordinary white loaf of bread.

The Vienna loaf was a very light porous loaf with the characteristic crust. It was made from a blended wheat flour with cottonseed oil, salt and yeast.

The Bohemian rye was from the same shop as the Vienna bread. This rye was very different from the usual rye loaf. It was made from a black rye flour

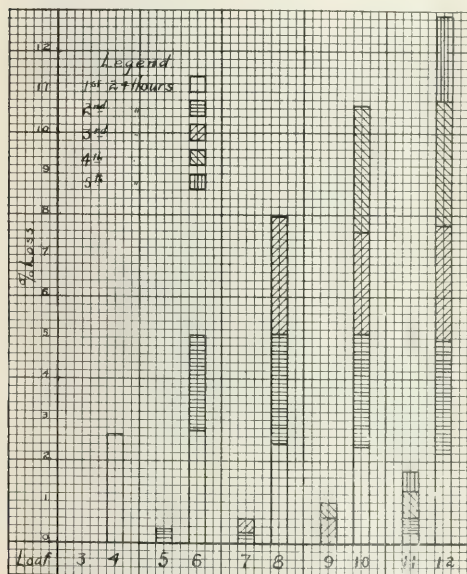


CHART 31—DAILY LOSS OF MOISTURE  
SET E—STRAIGHT DOUGH PAN BREAD

Odd numbered loaves wrapped in paraffin paper—Even numbered loaves unwrapped

with about 5 per cent wheat flour added. No shortening was used. The leavening agent was a mixture of sponge and a very little fresh yeast. A very small quantity of salt was added.

#### METHODS OF ANALYSIS

One of the difficulties incident to this investigation was the taking of proper samples. Preliminary investigations determined the fact that ordinary methods of sampling were not practical since the loss of moisture during preparation was so excessive as to invalidate the analytical results. The following method of procedure was finally employed with success: A loaf was divided crosswise and the crust separated from the crumb by taking off the outer layer in a slice just thick enough to include the browned portion. The

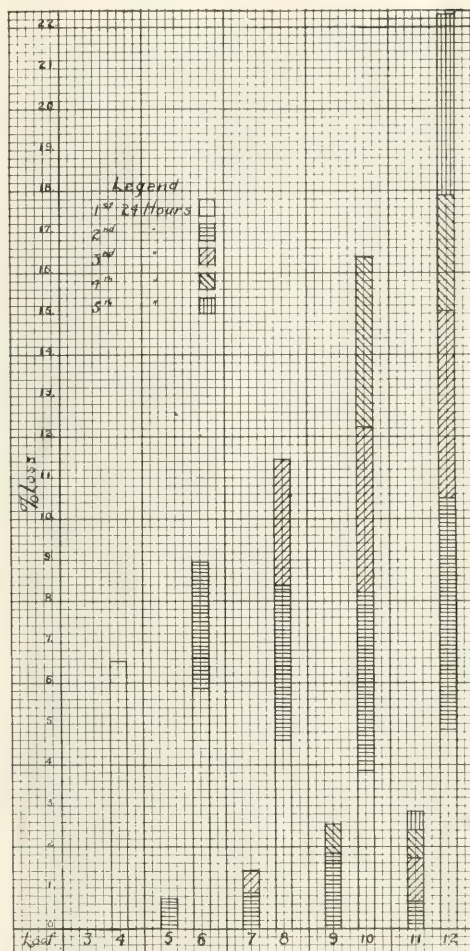


CHART 32—DAILY LOSS OF MOISTURE  
SET F—STRAIGHT DOUGH RYE BREAD

crust and crumb were then broken in large pieces and immediately dried to a water-free condition in an oven at a temperature of 98° C.

The drying, which was usually completed at the end of 12 hours, left the bread in a slightly browned, granular condition which was then reduced to a fine powder by grinding and passing through a forty mesh sieve. The prepared samples were then placed in tightly stoppered bottles from which the samples were taken for analysis after redrying for an hour to remove water taken up during the process of grinding.

The chemical methods employed were in general those found in *Bulletin 107*, Bureau of Chemistry, Department of Agriculture, together with modifications of some methods suggested by Jago.<sup>1</sup>

<sup>1</sup> Jago, W. and W. C., "The Technology of Bread Baking," 1911.



The moisture content was calculated from the loss in weight of the samples as they were prepared for grinding. This gave a very close approximation to the correct amount as the samples were large and the time between the time of cutting and weighing was nil.

The total proteids were calculated from the nitrogen determined by the Gunning modification of the Kjeldahl method upon a one gram sample of the dried crust or crumb using the factor 6.25.

The total carbohydrate content was determined upon a one-half gram sample by digesting for four hours in a ten per cent hydrochloric acid solution and then determining the sugar by Fehling solution.

The ash was taken on a one gram sample by igniting

gesting as in the total proteid determination. The evaporation of 20 cc. of the solution gave the soluble solids.

Soluble carbohydrates were taken by heating 20 cc. of the solution, 30 cc. distilled water and 5 cc. concentrated hydrochloric acid at the boiling temperature for four hours and then determining the sugars with Fehling solution.

The acidity was determined by titrating 20 cc. of the solution with  $N/20$  sodium hydrate and multiplying by the factor 0.05625 which gave per cent acidity as lactic acid.

The starch content was calculated by subtracting the soluble carbohydrate factor from the total carbo-

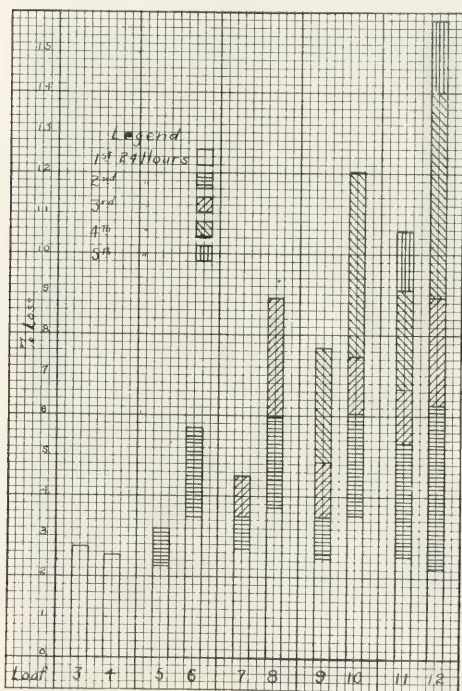


CHART 33—DAILY LOSS OF MOISTURE  
SET G—STRAIGHT DOUGH RYE BREAD

Odd numbered loaves wrapped in semi-porous paper—Even numbered loaves unwrapped

at low redness over a free flame. The soluble factors were determined upon a solution of the crumb or crust prepared according to Jago on page 768 using 10 grams of the dry sample instead of 25 grams. The sample was added to 250 cc. of distilled water and shaken vigorously for five minutes, and then allowed to stand for 25 minutes, making 30 minutes in all. The clear portion was decanted into a filter without putting the insoluble portion on the filter.

The soluble proteid content was determined by evaporating 100 cc. of the above solution to small quantity directly in the Kjeldahl flask and then di-

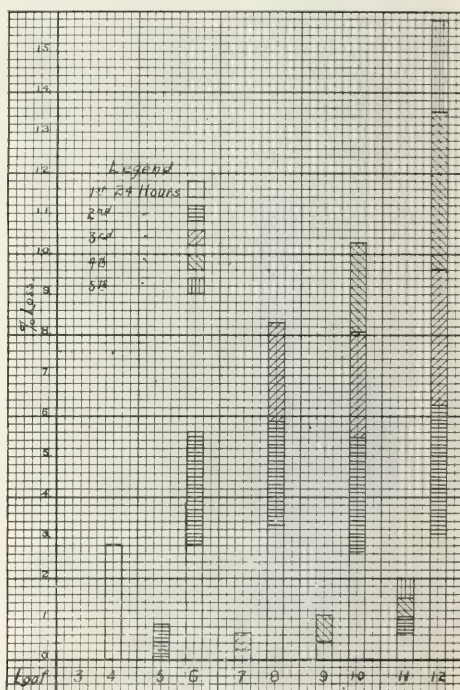


CHART 34—DAILY LOSS OF MOISTURE  
SET H—SPONGE DOUGH RYE BREAD

hydrate factor and converting the result by the starch factor 0.9.

#### THE CHEMICAL DATA ON WRAPPED AND UNWRAPPED BREAD

STRAIGHT DOUGH PAN BREAD—The moisture content of all the straight dough pan breads in the series dropped off uniformly both in the crust and crumb throughout the experiment as shown in Charts No. 29 to No. 36, inclusive. At the end of the sixth day the moisture content of the unwrapped loaf was a little higher than in the loaf wrapped in the semi-porous paper. In no case was there any evidence of trans-

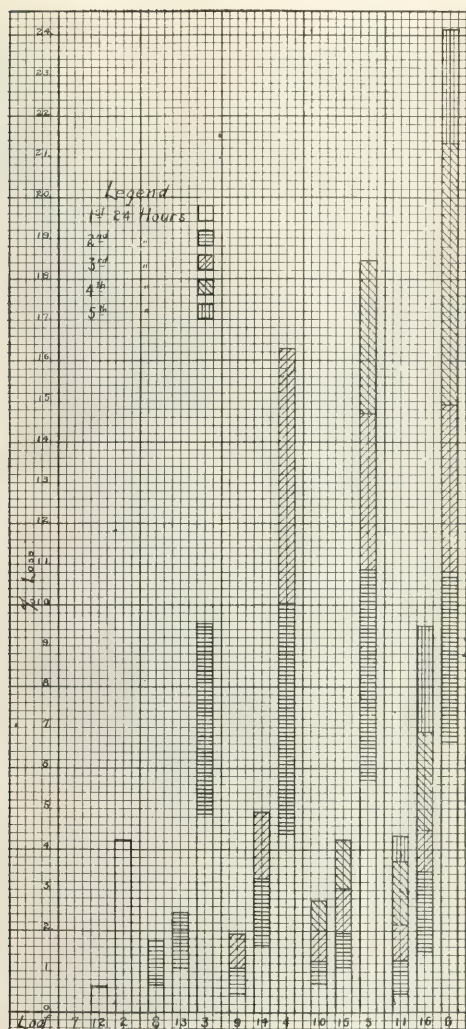


CHART 35—DAILY LOSS OF MOISTURE

SET I—STRAIGHT DOUGH VIENNA BREAD

Loaves 2, 3, 4, 5, 6—unwrapped; 7, 8, 9, 10, 11 wrapped in paraffin paper; 12, 13, 14, 15, 16—wrapped in semi-porous paper

tent of the crust of the waxed paper loaf. After the fourth day the soluble proteid content fell off sharply until the end of the experiment. There is no evidence of appreciable change in the gluten content which would be manifested by an increase of soluble proteids except that observed in the case of the unwrapped and semi-porous paper wrapped loaves, and in these cases the change is not sufficiently great to warrant the drawing of definite conclusions.

The soluble solid contents do not vary throughout the experiments.

The soluble carbohydrates contents vary so irregularly as to be of no real value. An important fact to be noted is that such change as was observed takes place uniformly both in the crust and crumb.

The starch contents do not vary greatly throughout the experiment.

The acidity content dropped off markedly in the case of the unwrapped loaf on the second day and

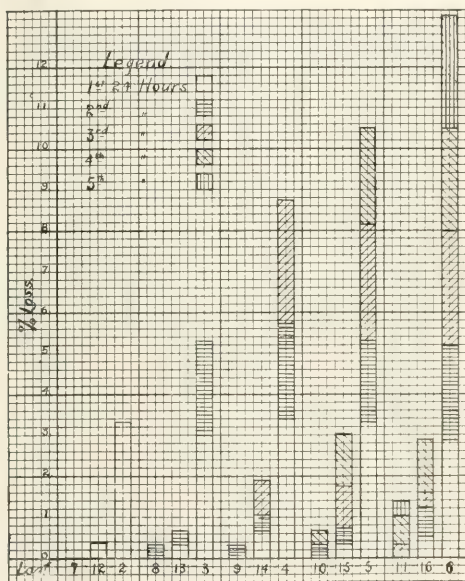


CHART 36—DAILY LOSS OF MOISTURE

SET J—SPONGE DOUGH BOHEMIAN RYE BREAD

Loaves 2, 3, 4, 5, 6—unwrapped; 7, 8, 9, 10, 11 wrapped in paraffin paper; 12, 13, 14, 15, 16—wrapped in semi-porous paper

ference of moisture from crumb to crust, the moisture content, as shown in the graphic curves (see Charts No. 24 to No. 27, inclusive), decreasing in the same proportion in the various loaves from day to day.

The total proteid content in all the loaves show no variation throughout the experiments.

The soluble proteid showed an increase on the third and fourth days in the case of the unwrapped and semi-porous paper wrapped loaves, and a sharp decrease on the third day in the loaf wrapped in the waxed paper. This decrease was followed on the fourth day by a decided increase in the soluble proteid con-

tent of the crust of the waxed paper loaf. After the fourth day the soluble proteid content fell off sharply until the end of the experiment.

The acidity of the loaf wrapped in semi-porous paper remained practically constant from the first to the sixth day. The acidity content of the waxed paper loaf decreased slightly on the third day and showed a slight increase in the crumb, on the fourth day followed by a decline at the end of the experiment. The ash content remained unchanged.

**STRAIGHT DOUGH RYE BREAD**—The moisture content in the unwrapped loaf on the first day after baking was, crust 26.4 per cent, crumb 40.4 per cent. The



moisture content of both crust and crumb dropped off regularly until the sixth day when the respective contents were 12.5 per cent and 32 per cent. A duplicate set of studies showed the moisture content as follows: crust 33.3 per cent, crumb 41.5 per cent on the first day and 14.2 per cent and 28.6 per cent on the sixth day. The daily loss in moisture was more constant on this set than on the first set, although, as reference to the chart shows, the loss of moisture in crust and crumb paralleled each other throughout the experiment. The loaves wrapped in the semi-porous and paraffin paper contained the same moisture content at the beginning but lost water more slowly and at the end of the experiment were still relatively soft. No transference of moisture from crumb to crust is shown save in the loaves wrapped in the waxed paper where the moisture loss in the crumb was relatively greater on the fourth and fifth days than in the loaves wrapped in semi-porous paper.

The total proteid content calculated to a dry basis showed no variation throughout the experiments either in the unwrapped or wrapped loaves.

The soluble proteids varied slightly from day to day but neither the figures nor the plotted curves show so much uniformity of action. The increase in soluble proteids was greater in the case of the unwrapped and paraffined wrapped loaf and less in the semi-porous paper.

The soluble solids content varied but slightly throughout the experiments.

The soluble carbohydrate content in general showed a slight decline toward the end of the period. On the third day an increase in soluble carbohydrates was noted in the bread in the semi-porous wrapper. Reference to the chart shows graphically the close parallel existing between the composition of the crust and crumb.

The total starch content varied but little throughout the experiment, the difference noted being due more to the fact that each day a different loaf was analyzed than to any change in composition due to ageing of the loaf.

The acidity content instead of increasing daily in the case of the unwrapped and waxed paper is lower on the second and third days, increasing very slightly on the fifth day. Almost no change is observed in the acidity of the loaves wrapped in semi-porous paper. The acidity of the crust and crumb, as shown by the graphic chart, parallel each other throughout the experiment.

The ash factors are of little value, the variation observed being due unquestionably to the difference in composition of different loaves from the same baking.

**STRAIGHT DOUGH VIENNA HEARTH**—The unwrapped Vienna hearth bread showed a rapid decrease in moisture content, both in the crust and crumb, the loss in crumb moisture, however, being greater than in the case of the crust. The loaves wrapped in semi-porous paper showed a slight drop in the crumb and after the third day a slight relative increase in the crust, the moisture content of the crust, however, being the same at the end as at the beginning of the experiment.

The moisture content of the waxed paper loaf showed a transference of moisture from crumb to crust on the second and third days, after that there being little change in composition.

The total proteid content showed no variation throughout the experiments.

The soluble proteid content on the third day showed an increase in the case of the unwrapped, but after that time a drop was observed. On the contrary, the soluble proteid content of the loaves wrapped in semi-porous and paraffin paper dropped uniformly both in the crumb and crust.

The soluble solid content remained unchanged through the experiments.

The soluble carbohydrates varied somewhat, the only uniformity of action being similarity of change in the crumb and crust.

The starch content remained nearly constant throughout the experiment, the difference noted being due to the fact that a different loaf was analyzed each day.

The lactic acid remained practically constant in the unwrapped loaf and in the waxed paper loaf. In the semi-porous wrapper, however, a slight increase was noted on the fifth and sixth days.

**SPONGE DOUGH BOHEMIAN RYE**—The moisture content of the unwrapped Bohemian rye breads dropped off uniformly from the first and the sixth days. There was no appreciable change in the moisture content of the loaves wrapped in the paraffin paper. The moisture content of the loaves in the semi-porous paper remained nearly constant in the crumb but dropped off slightly in the crust. But little transference of moisture from crumb to crust is noticed.

The total proteid content does not vary throughout the experiment.

The soluble proteid factor shows almost no change in the unwrapped loaf. It increases slightly in the semi-porous wrapped loaf on the second day, then falling off but reaching its highest figure on the sixth day. On the contrary, the loaves wrapped in paraffin paper showed practically no change until the sixth day when a slight falling off was observed in the crumb.

It will be noted that the soluble proteid content of the Bohemian rye bread is much higher throughout the experiments than in the case of the other breads examined.

The soluble solid and soluble carbohydrate and starch factors varied but slightly throughout the experiment.

The lactic acid acidity is high in the unwrapped loaf on the first day, falling off on the second day, and from there on showing no change. The loaf wrapped in paraffin paper shows practically no change during the six days. The loaf in the semi-porous wrapper shows but little increase of acidity on the third day and a falling off on the fourth day after which no change was observed.

#### BREAD WRAPPED HOT NOT STUDIED

It has been shown by Jacobs,<sup>1</sup> the authors and others,

<sup>1</sup> B. R. Jacobs, *Forecast*, 1912.



that bread wrapped while warm becomes soggy and of unpleasant flavor. The experience of bakers confirms these observations. In view of this admitted fact the authors have not felt it necessary to investigate the condition of bread wrapped fresh from the oven and all experiments have been conducted on bread allowed to cool thoroughly, usually during three hours after removal from the oven.

#### KIND OF PAPER WRAPPER USED IN WRAPPING BREAD

In these investigations the waxed or paraffin wrapper was a heavy paraffin paper which, as used, made an air-tight and moisture-proof package. The paper referred to as semi-porous was in part that used on the trade-marked "Holsum" bread and in part of the type furnished by Geo. W. Haffner. These wrappers, while affording satisfactory protection against dust and dirt, did not prevent the escape of moisture nor impair completely the circulation of air.

#### PHYSICAL APPEARANCE OF BREAD

Both baker and consumer judge the condition of bread by its physical appearance, that is, its odor, flavor and character of crust and crumb. The odor and flavor of distinct types of bread are essentially unlike. The crust of different types varies greatly, some breads being most desirable when the crust is light, soft and porous, while other types are preferred because of the thick and impervious crust. In order to determine the effect upon the physical appearance of the bread, we have exposed, under ordinary conditions of keeping, loaves unwrapped and wrapped with paraffin and semi-porous wrappers, and have noted each day the condition of the crust, the odor, taste and the development of moulds.

Five types of bread were used in the study: (1) straight dough pan bread; (2) straight dough rye bread; (3) sponge dough rye bread; (4) straight dough Vienna hearth; and (5) Bohemian rye sponge. The daily observations on each loaf are represented in the accompanying charts.

In general, the results confirm our earlier observations although the evidence of impaired condition in rye bread was not so great in this as in the earlier experiments.<sup>1</sup> The straight dough pan bread, (Sets C and D) developed a slightly stale odor on the second day, while the loaf in the paraffin wrapper was in excellent condition on the third day. The nutty flavor of the unwrapped loaf was about gone on the fourth day, while the wrapped loaf was still in fair condition.

Set "E" is a duplicate experiment with paraffin wrapped straight dough pan bread on bread obtained from a different source. In general the observations were the same as in Set "C."

The results on the straight dough pan bread in semi-porous wrapper were a little more favorable to the use of the wrapper than the paraffin wrapper. A very slight musty odor developed in the unwrapped bread on the 5th day. In the Vienna hearth straight dough studies, the unwrapped bread showed deterioration on the second day, the crust becoming increasingly hard and the crumb dry and tasteless. Where the

bread was wrapped in the paraffin paper the crust softened on the second day, but the odor and taste of the crumb remained good, no deterioration other than the softened crust being observed until the fourth day, when the crumb was noticeably stale.

The samples wrapped in the semi-porous paper were but little different from those wrapped in the paraffin. It was noted that the sample on the fourth day did not have as good a taste and odor as the duplicate sample wrapped in paraffin paper.

The authors' observations on the Vienna breads do not fully confirm their earlier report, these experiments showing that the Vienna hearth straight dough bread keeps reasonably well in both the paraffin and semi-porous paper.

The straight dough rye bread wrapped in paraffin paper preserved its condition both as to crust, odor and taste until the sixth day. The unwrapped bread showed a hardened crust on the second day and but little change in the condition of the crumb or in odor and taste until the fifth day. The straight dough rye bread in the semi-porous wrapper developed a stale odor on the fifth day. The unwrapped sample on this day had a very hard and dry crust, although the odor was still good.

The samples of sponge dough rye bread wrapped in paraffin paper were normal on the fourth day. On this day the odor and taste of the unwrapped samples were not as good as on the second day. On the sixth day the wrapped sample had a tough crust but the condition of the crumb, odor and taste was practically normal.

Samples of wrapped and unwrapped Bohemian rye sponge dough were decidedly influenced by wrapping. A sour taste was noticed on the third day on the unwrapped samples and the crumb was dried out. The crust of the sample wrapped in paraffin paper softened on the second day and on the third day. The loaf was moist and sticky and had a marked flavor. On the sixth day many mould colonies appeared on the crust, the crumb, however, being free from moulds. The loaf wrapped in semi-porous paper differed in no way from the loaf wrapped in the paraffin paper except that fewer mould colonies developed on the crust.

#### CONCLUSIONS

I—In general the chemical data confirm the authors' observations on the physical appearance of the wrapped and unwrapped loaves. Much of the chemical work shows no departure from established normals and the hundreds of analyses serve only to confirm each other. It is clear that the wrapping of bread, either in semi-porous waxed or paraffin paper retards the escape of moisture and tends to the preservation of the colloidal condition and physico-chemical equilibrium noted by Katz, the destruction of which results in staleness. The belief that the moisture of the crumb is imparted to the crust which thereby loses its crispness and becomes soft is not borne out by the results of the authors' experiments. Reference to the graphic charts show conclusively that in almost every case a loss of the moisture content of the

<sup>1</sup> Barnard and Bishop, Indiana State Board of Health Report, 1910, p. 234.

crumb is accompanied by similar and almost exactly parallel loss of the moisture content of the crust. Observations to the contrary have perhaps been in error because of the usual custom of comparing the feel of the wrapped and unwrapped loaves on successive days, instead of comparing the texture of the crust of the wrapped loaf with the crust of a freshly baked loaf. The authors' conclusions as to the loss of moisture, while somewhat surprising, appear to be fully justified by the results of the numerous experiments.

II—It has long been held that bread on keeping develops an increasing acidity which is customarily expressed as lactic acid. The work of White above referred to disputes this belief. The work of the authors shows conclusively that lactic acid acidity does not develop either in the unwrapped or wrapped loaf in the case of ordinary breads within six days after baking. A reference to the graphic chart clearly shows that the acid content remains almost constant, varying but little throughout the period during which the loaves were under observation.

III—The use of semi-porous and paraffin wrappers does not injure the quality of the loaf after the third day. Up to that time the keeping quality both as to condition of crumb, flavor and odor is enhanced by the use of the wrappers. Unwrapped bread loses its freshness after the first day. But little difference is observed in the condition of the straight dough pan bread, straight dough rye, sponge dough rye bread and straight dough Vienna hearth bread. Bohemian rye sponge dough wrapped or unwrapped bread is not of satisfactory quality on and after the third day.

DEPARTMENT OF FOOD AND DRUGS  
INDIANA STATE BOARD OF HEALTH  
INDIANAPOLIS

#### SOME DATA ON PEANUT BUTTER

By C. A. A. Urr  
Received June 1, 1914

Large quantities of shelled peanuts have been used during recent years for the manufacture of peanut butter. It is made in sanitary factories and packed in jars or tins holding from three ounces to five pounds.

The peanuts are shelled, roasted moderately, and then fanned to remove the outer covering. They are then reduced to a butter-like consistency by large grinders working on the same principle as the small family food grinder. From the grinder the butter is fed directly into a tin tube that fills the container. Some manufacturers salt their product; others market it unsalted. Packed in this manner it keeps almost indefinitely and makes a pleasant variety for luncheons, picnic menus, camping supplies, and regular household use.

In connection with the food control work of Kansas it was suggested that certain manufacturers were incorporating oils other than that occurring naturally in the peanut, in the manufacture of their peanut butter.

Samples of all the brands of peanut butter sold on the Kansas market were taken, in order that information might be obtained on this point. The following determinations were made:

- 1—Microscopic examination
- 2—Oil
- 3—Refractive index of the oil at 25° C.
- 4—Iodine number of the oil in some cases

The oil (fat) was determined by the official ether extraction method, using 2 grams of the butter and extracting with anhydrous ether. The Harding-Perkin method<sup>1</sup> was tried but an emulsion formed which would not break up, so we could not use it.

A larger quantity, 20 to 25 grams, was extracted with ether for use in determining the constants of the oil. Because of the smallness of the sample it was found impracticable to obtain the oil by pressing.

Microscopic examinations did not reveal the presence of any foreign starch in any of the samples.

TABLE I

Number	Brand	Percentage of oil	Refractive index at 25° C.	Iodine value (Hubb)
90497	Beechnut	49.12	1.4696	93.72
90498	Beechnut	54.02	1.4682	93.50
90499	Clubhouse	49.66	1.4685	"
90500	Heinz	46.44	1.4682	"
90501	Defiance	52.37	1.4696	94.36
90502	Puritana	49.32	1.4684	"
90503	Telmo	51.20	1.4682	"
90504	Beechnut	50.03	1.4707	92.40
90505	Royal	50.17	1.4684	"
90510	Rusdun	49.04	1.4680	"
90515	Lee	47.28	1.4685	"
90519	Derby	51.16	1.4684	"
90521	Bayle	52.63	1.4694	88.76
90522	Synms	52.60	1.4688	94.36
90524	Larkin	51.64	1.4682	"
90528	Pickwick	46.63	1.4682	"
90529	Sanburst	49.16	1.4680	"
90530	Orchid	50.67	1.4682	"
90531	Home Folk	50.16	1.4680	"
90532	Imperial	53.64	1.4690	93.40
90535	Punch	50.00	1.4682	"
90537	Monarch	47.18	1.4690	"
X-4	Armour	44.74	1.4690	88.04

Table I shows the results obtained on the peanut butter bought on the Kansas market. The percentage of oil varies from 46.44 per cent to 53.64 per cent. The refractive index varies from 1.4680 to 1.4707 at 25° C. The iodine number runs from 88.76 to 94.36.

Three samples of roasted peanuts reduced to butter-like consistency gave the following results:

Number	Percentage of oil	Refractive index at 25° C.	Iodine value (Hubb)
X-1	51.17	1.4685	89.9
X-2	52.03	1.4683	90.30
X-3	50.65	1.4683	88.75

A sample of raw peanuts, after shelling, was divided into four parts, which we designated as A, B, C, and D, and treated as follows:

A—Ground raw.

B—Heated at the temperature of boiling water in a steam oven for eight hours.

C—Heated in an electric oven at a temperature of 25° C. for eight hours.

D—Roasted brown in olive oil over a free flame and the excess of oil drained from it.

Each sample was ground separately and as finely as possible. These samples yielded the following results:

Sample	Percentage of oil	Refractive index at 25° C.
A	49.85	1.4672
B	51.09	1.4668
C	52.70	1.4674
D	55.48	1.4620

Leach, in "Food Inspection and Analysis," states

<sup>1</sup> THIS JOURNAL, 8, 843.

that peanuts contain 37.48 to 41.63 per cent of oil. Beattie, in *Farmers' Bulletin* No. 376, United States Department of Agriculture, says that the oil may run as high as 50 per cent in some peanuts. These results are evidently on the peanuts before roasting; after roasting the oil would be higher, due to a corresponding loss in water. Our results on the manufactured peanut butter do not show any more oil than may occur in the roasted peanut.

The U. S. standards for peanut, olive and cottonseed oils as given by Leach are as follows:

	Refractive index at 25° C.	Iodine value (Hübl)
Peanut.....	1.4690 to 1.4707	87 to 100
Olive.....	1.4660 to 1.4680	79 to 90
Cottonseed.....	1.4700 to 1.4725	104 to 110

The iodine value falls well within the limits of those given for pure peanut oil. The greatest variations are in the refractive index. Considering the fact that the oils obtained from the roasted peanuts give results comparable with the manufactured product, one could hardly say that oil had been added. That added oil can be detected is seen in the lowering of the refractive index by the use of olive oil.

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### THE INFLUENCE OF SULFUR ON SOIL ACIDITY

By H. CLAY LINT

Received June 2, 1914

The control of parasitic fungi which are capable of persisting in the soil has occupied the attention of many scientists and agriculturalists within recent years. To the above type of fungi belongs the one causing the ordinary scab of the potato. Even before this specific organism (*Oospora scabies*) had been isolated by Thaxter much work had been done toward devising methods of control.

Halstead<sup>1</sup> in the annual report of the New Jersey Experiment Station for 1895 reports favorable results in controlling the potato scab as a result of the application of flowers of sulfur to the soil. This work was not continued by Dr. Halstead, but within the last year the problem has been taken up again. It may be well at this time to state some of the facts that have been noted on a phase of the sulfur question relating to its effect on soil acidity.

Researches by M. A. Demolon<sup>2</sup> have shown that on soils of different origin, containing 3 per cent and 2.8 per cent, respectively, of calcium carbonate, there is a great increase in the amount of sulfates due to the addition of sulfur to the soil. He added 1 per cent of flowers of sulfur to these soils and incubated them at 20° C. for forty days. An analysis of the water extract gave these relative amounts of sulfates per hundred grams of soil as indicated by the weights of BaSO<sub>4</sub> given below.

	Gms. BaSO <sub>4</sub> With sulfur	Gms. BaSO <sub>4</sub> Without sulfur
Soil A.....	0.970	0.062
Soil B.....	0.612	0.047

Experiments by the same investigator demonstrated that the oxidation of sulfur was accomplished by bac-

teria in the soil. Brioux and Guerbet<sup>1</sup> have gone further and not only proven the bacterial nature of the action, but have furnished data on the influence of various substances—calcium carbonate, saccharose, peptone, etc., when added to the soil in which the sulfur was introduced.

In our recent work under field conditions where as much as 600 pounds of sulfur was applied per acre it was noticed that a large amount of the sulfur was still present in the soil at digging time, apparently in an unchanged condition. In order to ascertain facts on the rate of oxidation of the sulfur in the soil a series of tumblers containing 100 gram portions of soil were arranged, one-half containing sulfur, the other half without it. Thirty-three mg. of sulfur, equivalent to 1000 pounds of sulfur per acre foot (3,000,000 pounds), were added. The soils were made up to twenty per cent moisture content and covered with Petri dishes. By the addition of sterile water once a week the moisture content was practically constant throughout the experiment. One tumbler containing sulfur mixed with the soil and one not containing sulfur were removed each week and tested for acidity.

In this work the Jones<sup>2</sup> calcium acetate method of determining soil acidity was used. Preliminary tests comparing the Jones method with the Veitch method on a number of soils showed a close correlation, and as comparative results only were desired, this method was thought sufficiently accurate. In the following table are included the results of the analysis of this first series:

Time of incubation Weeks	Lime requirement in pounds CaO per 3,000,000 pounds of soil	
	Without sulfur	With sulfur
1	2347	2393
2	2347	2465
3	2250	2655
4	2393	3105
5	2404	3780
6	2538	4000
7	2565	4230
8	2538	4325
9	2465	4270
10	2160	3860
11	2430	4110

From the foregoing table it would appear that the sulfur had practically all been oxidized within the first eight or nine weeks. There is very little change in the acidity after the seventh week. Assuming that the Jones method has given the correct lime requirements it is interesting to note how closely the above lime requirements check up with the theoretical. An average of the lime requirements of the two soils from the seventh to the eleventh weeks inclusive gives 2431 pounds for the check and 4177 pounds for the sulfured soils. Obviously the difference of 1744 pounds of lime is due to the oxidation of sulfur. By means of the following proportion  $32 : 56 :: 1000 : x$  we find that the CaO equivalent to the 1000 pounds sulfur per acre would be 1750. Apparently the reason that no further increase in acidity takes place after the eighth week is due to the fact that all of the sulfur has been oxidized.

The fact that sulfur causes this increase in acidity

<sup>1</sup> *Compt. rend.*, **166** (1913), 1476.

<sup>2</sup> Reported at the 30th Annual Convention A. O. A. C., Washington, D. C., November, 1913.

<sup>1</sup> N. J. Exp. Station Rep., **1895**, p. 270.

<sup>2</sup> *Compt. rend.*, **166** (1913), 725.



under field conditions is shown by the following table in which are the analyses of soils from four old potato rows to which sulfur was applied last year. Samples were taken approximately one year after the application. The rows were 1400 feet long and borings 0-3 inches were made about every twenty feet. The sulfured rows ran consecutively but 12 rows were skipped before samples on the check row were taken. The sulfured rows were two feet eight inches apart.

Row	Rate of sulfur application Lbs. per acre	Lime requirement in lbs. CaO per acre
1.....	600	3187
2.....	300	2590
3.....	600	3025
4.....	300	2247
5.....	None (check)	883

Rows 1 and 2 received ammonium sulfate in the fertilizer last year, while rows 3 and 4 received sodium nitrate, a fact which would account for a difference in the acidity.

Laboratory experiments with a heavy clay loam soil and a sandy loam soil show a much more rapid oxidation of sulfur with the latter soil. Soils made up to water content (20 per cent) once each week and allowed to dry did not give as rapid oxidation as those kept covered so as to maintain optimum moisture content. The influence of texture, moisture and bacterial content will serve as a basis upon which further work on the influence of sulfur on soil reaction will be carried out.

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#### THE FERRIC ALUM ESTIMATION OF CASEINE<sup>1</sup>

By H. V. ARMY AND H. H. SCHAEFFER  
Received May 20, 1914

At the 53rd (1905) meeting of the American Pharmaceutical Association, one of us, with T. M. Pratt, presented a paper on a rapid estimation of caseine in milk based on precipitation of the casein with an excess of a solution of ferric alum of known titer, estimation of the unused iron in the filtrate and then calculating the amount of iron used by the caseine in the act of precipitation.

This paper was published in the Proceedings of the American Pharmaceutical Association, 53 (1905), 275, and in the *American Journal of Pharmacy*, 78 (1906), 121, but as our attention has been called to the fact that these two publications are not always conveniently accessible to the general chemical worker and as the paper was frankly a preliminary one, it seemed advisable to report further work on the topic and that in a strictly chemical journal.

In the previous paper was presented the method of manipulation and figures showing influence of temperature, of presence of fat (butter), of presence of sugar and, lastly, a few parallel experiments comparing the ferric alum figures with the Kjeldahl figures of the same sample of milk.

These latter figures, the attempt to express the value of 1 cc. of ferric alum solution in terms of nitrogen and of caseine, were not sufficiently exact nor were the number of assays performed sufficient for

a positive statement of the ferric alum factor. While the process in the empiric commercial milk testing work for which it was devised proved entirely satisfactory, proof of its scientific accuracy was yet to be shown; and this has been the aim of our experiments during the past winter.

Since the publication of our prior paper, VanSlyke & Bosworth<sup>1</sup> have published a titration method based on use of tenth-normal alkali. This plan has not proved as satisfactory in our hands as the ferric alum method but the fact has no bearing on our investigation, since there is room for more than one simple estimation of caseine.

#### THE FERRIC ALUM ESTIMATION

Since the publication of our previous paper, several modifications of the process as originally published have suggested themselves and have been tried out. In all the work we have used as the standard iron solution, a ferric alum containing 48.2224 g.  $\text{Fe}(\text{NH}_4)(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  to the liter, standardizing this solution by the usual method of volumetric ferric estimation; adding potassium iodide and hydrochloric acid and titrating the liberated iodine with tenth-normal sodium thiosulfate. One cc. of our standard solution, therefore, liberates 12.692 mg. iodine which in turn requires 1 cc. tenth-normal sodium thiosulfate for decolorization. In our previous work, in an attempt to dispense with the use of the rather costly potassium iodide, we have repeatedly tried estimation of the iron solution by titration with tenth-normal alkalis, noting end of reaction by use of phenolphthalein as indicator. In this case the ferric alum solution (48.2224 g. to 1000 cc.) was standardized by titration against tenth-normal sodium hydroxide, 1 cc. of ferric alum solution taking 3 cc. tenth-normal alkali for complete neutralization. This, we found an easier procedure than would seem at first glance, as after a little experience, it is not difficult to note the red tint of the alkaline phenolphthalein combination in the supernatant liquid about the ferric hydroxide precipitate. The figures of such a line of assays in which the excess of ferric alum was estimated with  $N/10$  alkali are given below.

#### COMPARISON OF THIOSULFATE ASSAYS WITH NORMAL ALKALI ASSAYS

In this and all other experiments described in this paper, the ferric alum solution employed was one containing 48.2224 g.  $\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  to the liter and 1 cc. of this solution represented 1 cc.  $1/10$   $N$  sodium thiosulfate solution or 3 cc.  $1/10$   $N$  sodium hydroxide solution and in the rest of this paper this solution will be called the standard ferric solution.

Five cc. of milk were mixed with 5 cc. of this standard ferric alum solution, the mixture filtered, the precipitate washed free from water-soluble iron and amount of iron in the filtrate and washings were estimated either with tenth-normal thiosulfate or with tenth-normal alkali. The results of such parallel assays from same samples of milk are here tabulated.

(a) Five cc. milk with 5 cc. ferric alum and the

<sup>1</sup> THIS JOURNAL, 1 (1909), 768.

<sup>1</sup> Presented at the 48th Meeting of the American Chemical Society, Rochester, September 8-12, 1913.

filtrate titrated with  $N/10$  thiosulfate. Five cc. ferric alum = 5 cc.  $N/10$  thiosulfate.

(b) Five cc. milk with 5 cc. ferric alum and the filtrate titrated with  $N/10$  NaOH. Five cc. ferric alum = 15 cc.  $N/10$  NaOH.

	a			b		
	Cc. thio used by filtrate	Representing ferric alum sol.	Cc. ferric alum consumed	Cc. NaOH used by filtrate	Representing ferric solution	Cc. ferric sol. consumed
1 A.....	2.5	2.5	2.5	7.7	2.57	2.43
1 B.....	2.5	2.5	2.5	8.4	2.80	2.20
2 A.....	2.6	2.6	2.4	6.9	2.3	2.70
2 B.....	2.7	2.7	2.3	6.1	2.03	2.97
3 A.....	2.6	2.6	2.4	7.6	2.53	2.47
3 B.....	2.6	2.6	2.4	8.0	2.67	2.33
4 A.....	2.7	2.7	2.3	6.0	2.0	3.0
4 B.....	2.6	2.6	2.4	6.1	2.03	2.97
5 A.....	2.7	2.7	2.3	7.9	2.63	2.37
5 B.....	2.7	2.7	2.3	6.1	2.03	2.97

From the above tabulation it is seen, as might have been expected, the assay of the iron filtrate with potassium iodide, and tenth-normal thiosulfate gave more accurate results than titration with alkali, even when the milk is strictly fresh. But in some cases the assay with alkali is very convenient.

Our next work was a comparison of the ferric alum-thiosulfate estimation with Kjeldahl-Gunning nitrogen estimations of the same milk. The ferric alum estimation was conducted with about 5 g. milk, carefully weighed in a Kjeldahl digesting flask, 20 cc. standard ferric alum solution added, the filtrate and washings treated with 3 cc. 31 per cent hydrochloric acid and 3 g. potassium iodide, the solution digested in water bath at  $40^\circ$  for 30 minutes and then titrated with tenth-normal sodium thiosulfate which had been standardized against C. P. potassium dichromate.

The nitrogen assays were performed on the caseine iron precipitate adhering to the Kjeldahl flask, and that portion which was washed upon a filter, the entire precipitate being carefully washed free from soluble iron and the nitrogen of filter paper being controlled by using similar paper in the blank experiments which were run with every set of milk used. As none of the blanks required more than 0.1 cc. of  $N/10$  acid to neutralize distillate, they are not figured in the tables which follow.

The Kjeldahl-Gunning method employed was that described in U. S. Department of Agriculture, Bureau of Chemistry, *Bulletin 107* (1911), and the distillations were conducted in a Sy apparatus. Certified pipettes and burettes were employed in all of these assays. The results of the first batch of these comparative assays are tabulated below.

#### COMPARISON OF FERRIC ALUM-THIOSULFATE WITH KJELDAHL FIGURES

(a) Milk (about 5 cc.) mixed with 20 cc. standard ferric solution and titrated with  $N/10$  thio. Twenty cc. standard ferric solution = 20 cc.  $N/10$  thiosulfate.

(b) Precipitate from same milk assayed for nitrogen by Kjeldahl-Gunning process. One cc.  $N/10$   $H_2SO_4$  = 0.001401 g. nitrogen = 0.00893838 g. casein.

Examination of the figures show so wide a variation in the ferric alum-caseine factor as to suggest their absolute worthlessness, but a more careful study shows that the discrepancy is more apparent than real,

that it is due to the use of a thiosulfate of too great a strength.

One cc.  $N/10$  thiosulfate = 0.0482224 g. iron.  
Hence 0.1 cc. of  $N/10$  thiosulfate = 0.00482224 g.

Milk sample	Wt. milk.	b			a			Value of 1 cc. ferric sol. in g. caseine
		Cc. $N/10$ $H_2SO_4$ consumed	Per cent N	Per cent caseine	Cc. ferric sol. consumed	No. cc. thio used		
1 A.....	5.0569	16.4	0.454	2.895	2.3	17.7		0.06365
1 C.....	5.36	18.3	0.466	2.941	2.7	17.7		0.06056
3 C.....	5.342	17.7	0.464	2.96	2.7	17.3		0.05856
4 A.....	5.9801	19.3	0.466	2.973	3.2	16.8		0.05555
4 B.....	4.923	16.0	0.455	2.903	2.3	17.7		0.06213
4 C.....	6.1	19.8	0.455	2.903	3.0	17.0		0.05903
5 A.....	5.003	16.7	0.468	2.986	2.5	17.5		0.05976
5 B.....	4.9861	16.5	0.464	2.96	2.5	17.5		0.05904
6 A.....	5.2963	17.1	0.453	2.89	2.4	17.6		0.06128
6 B.....	4.06	13.1	0.452	2.884	1.9	18.1		0.06163
6 C.....	6.105	19.3	0.443	2.826	3.0	17.0		0.05751
7 A.....	4.9911	16.9	0.474	3.024	2.2	17.8		0.06861
7 C.....	5.924	19.7	0.466	2.973	3.2	16.8		0.05504
8 A.....	5.3691	17.9	0.467	2.979	2.3	17.7		0.06934
8 B.....	6.0136	19.9	0.463	2.954	3.2	16.8		0.05351
8 C.....	4.09	13.3	0.455	2.903	2.0	18.0		0.05937
9 A.....	6.1001	19.6	0.450	2.871	3.0	17.0		0.05838
9 C.....	5.369	16.9	0.441	2.814	2.4	17.6		0.06295
10 A.....	4.9931	17.3	0.486	3.101	3.3	17.7		0.06321
10 B.....	5.871	19.6	0.468	2.986	2.9	17.1		0.06045
10 C.....	4.8654	16.3	0.469	2.998	2.3	17.7		0.06342
11 A.....	4.065	12.6	0.444	2.769	1.9	18.1		0.05924
11 B.....	5.1131	16.2	0.434	2.835	2.4	17.6		0.06035
12 A.....	6.113	20.0	0.458	2.922	3.2	16.8		0.05582
12 C.....	5.0365	17.0	0.473	3.018	2.4	17.6		0.06251
13 A.....	6.0156	20.3	0.473	3.018	3.3	16.7		0.05502
13 B.....	4.998	17.5	0.490	3.126	2.6	17.4		0.06009

iron, and the difference in our thiosulfate figures of only 0.1 cc. when used in above calculations means a discrepancy in the ferric alum-caseine figure greater than is permissible in careful analytical practice. For instance, a difference of 0.1 cc.  $N/10$  thio solution would be equivalent to a difference of approximately 0.006 g. casein which is in excess of permissible error when we figure that we used about 5 cc. milk in each experiment containing approximately 0.125 g. caseine (2.5 per cent) which would mean that an error of 0.006 g. caseine (or 0.1 cc.  $N/10$  thio solution) represents 4.8 per cent of the total caseine present.

This defect was remedied by the simple expedient of changing the amount of standard iron solution used and employing a fiftieth-normal instead of a tenth-normal thiosulfate solution.

Therefore, in the final run of comparative assays, we employed about 5 g. milk (exactly weighed), 5 cc. standard iron solution (48.2224 g. to liter) and after adding to the filtrate 3 cc. 31 per cent HCl and 2 g. potassium iodide, we titrated with  $N/50$  thiosulfate solution, each cc. of which represented 0.00064448 g. iron. The results are tabulated below.

Examination of the following table shows that under precautions observed, the relationship of the amount of ferric alum absorbed by the milk and the nitrogen (and deduced caseine) value of the milk by the Kjeldahl-Gunning method is practically within the limits of analytical deviation. It will be noted that in the 46 assays reported, ten showed that 1 cc. standard iron solution represents 58 to 59 mg. of caseine, 34 show 59 to 60 mg. caseine, while only two show deviation from these figures. Hence we feel justified in striking the average of our results tabulated above and stating that 1 cc. of standard iron solution [48.2224 g. of  $FeNH_4(SO_4)_2 \cdot 12H_2O$  to 1000 cc.] precipitates from milk 0.05934 g. casein.

As to manipulative details, the assay we published in 1905 had the one disadvantage that separation of

the precipitate from the filtrate and particularly by washing the precipitate free from soluble iron, was a tedious process, covering at least a half hour under the most favorable conditions of filtration. Efforts have been made to reduce time of operation and considerable success has been attained.

# RELATION OF TITRATION OF COMPLETE WASHINGS AND OF ALIQUOT PARTS

## RELATION OF TITRATION OF COMPLETE WASHINGS AND OF ALIQUOT PARTS Added 10 cc. ferric solution to each

Used milk	Cc. N/10 thio for total	Cc. thio for (50 per cent) aliquot part
A 10 cc. ....	5.1	2.9
B 10 cc. ....	5.0	2.7
C 10 cc. ....	5.2	3.0
D 10 cc. ....	4.9	2.8
E 10 cc. ....	5.1	2.9
F 10 cc. ....	4.9	2.7
G 10 cc. ....	5.2	3.0
H 10 cc. ....	4.9	2.5
I 10 cc. ....	5.0	2.9
J 10 cc. ....	4.8	2.9

Sample No.	Wt. milk	The Kjeldahl assay				The ferric alum and thiosulfate assay			
		No. cc. N/10	Per cent H <sub>2</sub> SO <sub>4</sub>	Per cent casein	Per cent sol.	No. cc. ferric sol.	Cc. thio consumed	Cc. solution in g.	Value of 1 cc. ferric casein
1 A.....	5.913	19.1	0.452	2.884	2.86	10.7	0.05963		
1 B.....	5.431	17.5	0.448	2.858	2.5	11.9	0.05935		
1 C.....	7.26	23.5	0.453	2.89	3.54	7.3	0.05927		
2 A.....	6.1381	20.1	0.458	2.922	3.04	9.8	0.05899		
2 B.....	5.212	16.8	0.451	2.877	2.53	12.3	0.05903		
2 C.....	4.6891	15.2	0.454	2.897	2.28	13.6	0.05958		
3 A.....	5.621	18.0	0.448	2.858	2.7	11.5	0.05949		
3 B.....	5.1312	17.9	0.489	3.12	2.68	11.6	0.05976		
3 C.....	6.12	19.8	0.453	2.89	2.98	10.1	0.05935		
4 A.....	5.131	21.2	0.469	2.927	2.6	10.1	0.05927		
4 C.....	4.1219	13.3	0.452	2.884	2.02	14.9	0.05885		
5 A.....	6.421	21.1	0.460	2.935	3.2	9.0	0.05917		
5 B.....	5.1312	16.8	0.459	2.928	2.58	12.1	0.05862		
6 A.....	7.1691	25.2	0.452	2.852	3.4	8.0	0.06014		
6 B.....	6.51	20.9	0.450	2.871	3.12	9.4	0.05990		
6 C.....	7.8131	25.2	0.452	2.884	3.74	6.3	0.06025		
7 A.....	4.9361	16.0	0.454	2.897	2.44	12.8	0.05861		
7 C.....	5.121	16.7	0.457	2.916	2.52	12.4	0.05927		
8 A.....	4.8262	15.6	0.453	2.89	2.34	13.3	0.05961		
8 B.....	6.131	20.1	0.459	2.928	3.06	9.7	0.05868		
8 C.....	4.9361	16.1	0.457	2.916	2.42	12.9	0.05948		
9 A.....	5.426	17.3	0.447	2.852	2.6	12.0	0.05952		
9 B.....	6.4289	20.7	0.451	2.877	3.12	9.4	0.05928		
9 C.....	7.1101	22.6	0.445	2.839	3.4	8.0	0.05937		
10 A.....	5.1324	16.7	0.456	2.909	2.52	12.4	0.05925		
10 B.....	6.1203	19.2	0.451	2.877	2.98	10.1	0.05929		
10 C.....	4.9132	16.1	0.459	2.928	2.4	13.0	0.05994		
11 A.....	5.654	18.2	0.451	2.877	2.76	11.2	0.05893		
12 A.....	6.3521	20.4	0.449	2.865	3.08	9.6	0.05909		
12 B.....	5.013	19.8	0.453	2.89	2.98	10.1	0.05935		
12 C.....	5.9916	19.3	0.451	2.877	2.99	10.5	0.05944		
13 A.....	4.3571	14.2	0.457	2.916	2.14	14.3	0.05937		
13 B.....	4.1361	13.5	0.457	2.916	2.02	14.9	0.05971		
13 C.....	7.013	22.7	0.453	2.89	3.44	7.8	0.05892		
14 A.....	6.1251	19.6	0.448	2.858	2.92	9.4	0.05995		
14 B.....	5.989	19.3	0.451	2.877	2.88	9.6	0.05883		
15 A.....	6.1251	19.6	0.448	2.858	2.96	10.2	0.05912		
15 B.....	5.1369	16.8	0.452	2.884	2.85	12.5	0.05926		
16 A.....	4.9812	16.2	0.455	2.903	2.44	12.8	0.05926		
16 C.....	6.71	21.8	0.455	2.903	3.26	8.7	0.05975		
17 B.....	5.0091	16.1	0.450	2.871	2.44	12.8	0.05894		
17 C.....	4.327	14.2	0.459	2.928	2.14	14.3	0.05920		
18 A.....	5.6631	18.1	0.448	2.858	2.72	11.4	0.05950		
19 A.....	4.986	16.1	0.452	2.884	2.44	12.8	0.05893		
19 B.....	4.3521	14.2	0.457	2.916	2.14	14.3	0.05930		
19 C.....	4.32	14.1	0.457	2.916	2.10	14.5	0.05999		

One way to save time that has been employed in other casein assays was by the titration of an aliquot part of the filtrate, rather than the entire filtrate and washings from the precipitate, but the plan, while quick, did not appeal to us on the score of accuracy.

In order to see whether titration of an aliquot part would be as exact as titration of the entire filtrate, a line of comparative assays from the same milk was performed. In each case 10 cc. of milk were mixed with 10 cc. standard ferric iron solution and the filtrate titrated for ferric iron by the usual KI-thiosulfate method, described above. But in one case the entire filtrate and washings were titrated, while in the other case the milk-iron mixture was brought to a definite volume (100 cc.), and this filtrate, representing half of this volume (or 50 cc.) and presumably representing half of the milk used (or 5 cc.), was titrated. The figures given below show what might have been expected, that such aliquot 50 per cent part does not represent 50 per cent of the milk employed, since in such reasoning no consideration is taken of the bulk of the precipitated casein of all the milk, which remains in the untitrated portion.

Our present method of assay differs from that published in 1905 only in respect to the two important improvements of greater accuracy and less time required. Accuracy is secured by use of N/50 thiosulfate solution and time-saving is accomplished by hastening filtration and washing. In our prior work we had tried rapid (suction) filtration without much success, but in our recent experiments we have very materially lessened duration of the assay by use of quick filtration. At first we mixed the milk with purified talc. (U. S. P.) and with a pure form of kieselguhr (2 g. to each 5 cc. milk) running blank assays to see if the diluent employed had any influence in the iron figure. Finding the diluent of no influence, by employment of a water suction pump, aspirating bottle, porcelain perforated filtering disc and small disc of filter paper we reduced the time of filtration and washing from 30 to 60 minutes down to 15 minutes. Later we found we could filter as rapidly with straight iron curd without the diluent, especially if the milk and iron mixture was allowed to stand an hour before filtration. Our present method of assay may, therefore, be described as follows:

About 5 cc. (or g.) milk are mixed with 5 cc. standard ferric solution (4.2224 g. per liter) and allowed to stand an hour; the mixture is then filtered by use of filtering disc and funnel, aspirating bottle and water suction pump and the precipitate washed until washings are free from iron as shown by "spotting test" with potassium ferrocyanide. Freedom from iron is usually shown after 200 cc. of combined filtrate and washings are obtained and when suction filtration is employed the washing is finished within fifteen minutes.

The filtered fluid is placed in an appropriate glass stoppered flask, 3 cc. 31 per cent HCl and 2 g. KI are added, the mixture digested at 40° C. for 30 minutes and the free iodine is titrated with N/50 thiosulfate solution, starch paste being used as indicator after the fluid has been decolorized to a faint straw tint.

Our figures show that if 6.12 g. milk take 2.98 cc. standard ferric solution, employment of the iron-casein-factor deduced above indicates that the 6.12 g. of that milk contains 0.17683 g. (2.98 × 0.05934) casein; that it, therefore, contains about 2.889 per cent casein.

Examination of the method just given shows that the actual time consumed in the assay is 35 minutes, distributed as follows: Mixing milk and standard ferric solution, 5 minutes; filtering and washing mixture, 15 minutes; adding KI and HCl, 5 minutes; final titration, 10 minutes. In addition an hour's



maceration of the ferric-milk mixture and 30 minutes digestion of the ferric-KI mixture before titration means an assay occupies about two and a half hours. If we hasten, however, the maceration during an hour can be omitted (as little as 20 minutes will suffice) and as cited above, where haste is more essential than strict accuracy the filtrate can be immediately titrated for iron by use of  $N/10$  alkali, thus reducing the entire operation to a matter of less than an hour. If titration with alkali is followed, it is, of course, essential that the natural acidity of the milk be taken into consideration.

Recently we have endeavored to apply the method to dry technical caseine, but so far without satisfactory results. The first work—maceration of the dry caseine with a definite quantity of standard ferric solution and subsequent titration of the filtrate and washings with  $N/10$  thiosulfate solution—gave no uniform results whatever; but when the caseine was dissolved in alkali before treatment with the standard ferric solution, fairly good results were obtained.

In the operation, approximately 0.6 g. caseine was carefully weighed, dissolved in 25 cc.  $N/10$  NaOH solution which had been previously standardized both against acid and against the standard ferric solution. Enough of this solution (8.3 cc.) to combine with all of the alkali was added, followed by 25 cc. of the standard ferric solution (33.3 cc. in all) after which the mixture was macerated for 30 minutes.

It was then filtered and the filtrate and washings were then titrated with  $N/10$  thiosulfate solution with the following results:

#### FERRIC ALUM-THIOSULFATE ESTIMATION OF DRY CASEINE

One cc. standard ferric solution = 3 cc.  $N/10$  NaOH solution = 1 cc.  $N/10$  thiosulfate solution.

Sample number	Wt. caseine	Cc. thio used	Cc. ferric solution consumed	Equivalent of 1 cc. ferric sol. expressed in g. caseine
1.....	0.6014	12.7	12.3	0.0488
2.....	0.6002	14.2	10.8	0.0555
3.....	0.6130	11.2	13.8	0.0444
4.....	0.6100	12.1	12.9	0.0472
5.....	0.5991	11.3	13.7	0.0437

Average (all estimations were from batch of dry caseine) 0.0479.

These figures do not agree very well with the factor deduced above—1 cc. standard ferric solution = 0.059 g. caseine—but they are near enough to suggest that further work may bring results of practical value.

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## STUDIES IN SYNTHETIC DRUG ANALYSIS

### II—ESTIMATION OF ANTIPYRIN<sup>1</sup>

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In studying the action of an aqueous solution of iodine on antipyrin, Manseau<sup>2</sup> found that a relatively small, but constant quantity of iodine was absorbed, which behavior he proposed to utilize as a basis for

<sup>1</sup> This method is inapplicable to preparations containing caffeine and pyridine. The latter substance, however, very rarely occurs in admixture with antipyrin. A method for the estimation of antipyrin and caffeine in admixture is in course of preparation for publication.

<sup>2</sup> Bull. Soc. Pharm. Bordeaux, 1889, p. 148.

the proximate assay of antipyrin. He noted the fact that apparent substitution took place until a point was reached when further addition of iodine produced a tarry precipitate, but no attempt was made to ascertain the nature of the compounds formed.

More satisfactory results were obtained by Schuyten,<sup>3</sup> who titrated very small amounts of antipyrin in relatively large volumes of water (20 to 30 mg. in 1000 cc.) with an aqueous solution of iodine (approximately 0.02  $N$ ).

Kippenberger<sup>2</sup> investigated the availability of Wagner's reagent (an aqueous solution of iodine and potassium iodide) in alkaloidal estimation as well as that of antipyrin. He reported a method for this substance which he claimed to be entirely satisfactory, consisting in the precipitation of antipyrin from acid solution with an excess of Wagner's reagent, as an iodine addition product or periodide of tarry consistency, and then in titrating the unexpended iodine in an aliquot of the filtrate with sodium thiosulfate, thus determining, by difference, the iodine consumed in periodide formation. His method is based on the assumption that each molecule of antipyrin combines with a molecule each of hydriodic acid and iodine to yield the compound  $C_{11}H_{12}N_2O.HI.I_2$ , under all conditions, provided an excess of iodine is used. A few years later, Stolz<sup>2</sup> declared Kippenberger's method to be practically worthless and his analytical data untrustworthy, whereupon a lengthy controversy ensued,<sup>4</sup> in the course of which Kippenberger was forced to admit that certain inaccuracies were indeed inherent in his method, but he still claimed its practicability, provided the reagent is standardized against antipyrin under conditions similar to those of subsequent determinations.

While making an exhaustive study on the interaction of antipyrin and iodine under a variety of conditions, as also on the several compounds produced thereby, we have, ourselves, obtained results fully substantiating the criticisms advanced by Stolz and demonstrating beyond the possibility of doubt that Kippenberger's theory of periodide formation in general and his antipyrin method in particular are absolutely untenable. Details of this work we expect to present for publication in the near future.

A distinct improvement over the procedure as suggested by Manseau was made by Bougault<sup>5</sup> who caused the antipyrin and iodine (standardized against pure iodine) to react in alcoholic solution and in the presence of mercuric chloride, thereby effecting an absorption of approximately 1 molecule of iodine for every molecule of antipyrin involved. Notwithstanding Fernau's<sup>6</sup> inability to obtain satisfactory results with the method as perfected by Bougault, Zernik<sup>7</sup> employed it with advantage in the estimation of antipyrin in combinations like migranin (antipyrin-caffeine-citric acid),

<sup>1</sup> Schuyten, Chem. Ztg., 19 (1895), 1786.

<sup>2</sup> Z. anal. Chem., 35 (1896), 659.

<sup>3</sup> Arch. Pharm., 237 (1899), 71.

<sup>4</sup> Z. anal. Chem., 38 (1899), 230, 278, 280; Arch. Pharm., 238 (1900), 135, 301.

<sup>5</sup> J. pharm. Chim., 1 (1898), 858.

<sup>6</sup> Z. d. allg. Oester. Apoth. Vereins, No. 2 (1904).

<sup>7</sup> Apoth. Ztg., 21 (1906), 686.

and we have likewise found it of value in the analysis of certain mixtures if applied in slightly modified form.

Now it has been noted by Bougault that, when a neutral aqueous solution of antipyrin is treated with iodine and the liquid kept neutral or even slightly alkaline by an antiacid like sodium acetate,<sup>1</sup> or better, according to our own experience, sodium bicarbonate, a reaction takes place whereby the primarily formed di-iodoantipyrin splits off a molecule of hydriodic acid with the result that an atom of hydrogen in the antipyrin is substituted by an equivalent of iodine, thus yielding iodoantipyrin,  $C_{11}H_{11}N_2IO$ , identical with the substance first prepared by Dittmar<sup>2</sup> from antipyrin and iodinetrichloride. In a strongly mineral acid solution, however, there is practically no substitution. Iodoantipyrin is moderately soluble in boiling, but only sparingly so in cold water.<sup>3</sup> In alcohol and chloroform it dissolves quite readily. A method proposed by the British Pharm. Codex (1908) and based on the slight solubility of this iodine derivative in aqueous media involved its precipitation and subsequent weighing. As might be expected, the results were radically low and quite unreliable. An alleged improvement on the Codex procedure is suggested by Astre<sup>4</sup> and involves the use of an empirical factor, which takes into account a correction for the partial solubility of iodoantipyrin in water. This, however, is quite as unsatisfactory, in that it holds good only for conditions which are described, but which in unknown solutions could obtain only by accident.

In the course of our studies on antipyrin and its iodine derivative, we have found that the latter compound can indeed be made to serve as the basis for a very exact determination of the parent substance, provided the iodoantipyrin is isolated not by filtration but by extraction with chloroform. The chloroformic residue dried at  $110^\circ$  gives an accurate index to the quantity of antipyrin contained in the original solution or mixture under investigation. While we can claim no unusual advantage for this method over one based on Bougault's procedure (titration with standard alcoholic iodine), it can nevertheless serve the useful purpose of an independent method and control. As developed in this laboratory, the method is applicable to the estimation of antipyrin when alone or in admixture with acetanilide, phenacetin, sulfonal or any water-soluble organic compound incapable of yielding an insoluble iodine derivative under the conditions prescribed. The separation of antipyrin from any such compounds depends on the fact that, in aqueous-acid solution, iodine precipitates the antipyrin as a periodide in tarry form, which is filtered and washed, then dissolved in methyl alcohol and, on treatment with sodium bicarbonate, converted to iodoantipyrin, the excess of iodine being subsequently removed by sodium thiosulfate. After extraction with chloroform, drying at  $110^\circ$  and weighing, the antipyrin is calculated

from the weight of iodoantipyrin by means of the appropriate factor.

**METHOD I**—Antipyrin alone present, or in such admixture that after treatment with iodine, no substance other than iodoantipyrin will be extracted by chloroform:

Into a separatory funnel of about 150 cc. capacity, introduce the sample containing not more than 0.25 g. of antipyrin, add 20 cc. of water (in which the antipyrin may have been previously dissolved), 5 cc. of washed (alcohol-free) chloroform, 0.5 g. of sodium bicarbonate and 15 to 20 cc. of approximately 0.2 *N* iodine (or an equivalent of 0.1 *N* iodine), or just sufficient to insure, after vigorous and continued agitation, an excess of unexpended iodine in liquid contents of separator. Shake mixture at intervals for a period of 5 minutes, then discharge the free iodine with a few drops of conc. solution of sodium thiosulfate. Extract the resulting iodoantipyrin with three 25 cc. portions of chloroform, washing each portion successively in a second separator with 5 cc. of water, then withdraw solvent through a small (5.5 cm.) dry filter into a tared 50 cc. beaker and evaporate by means of an air blast, or by heating on steam or vapor bath. Dry the residue in oven one-half hour at  $110^\circ$ , cool and weigh. Multiply weight of iodoantipyrin by the factor 0.5992 to obtain amount of antipyrin present.

Should it seem desirable to recover most of the chloroform required in above operations, withdraw the several portions into a tared 200 cc. Erlenmeyer instead of a beaker, distilling off the solvent by gentle heat until only about 5 cc. remain. Then evaporate this on steam bath as above. Care should be taken to recover all traces of iodoantipyrin likely to collect about tip of delivery tube of separator as well as on the rim of filter.

**METHOD II**—Antipyrin in admixture with acetanilide, phenacetin, sulfonal or other substance incapable of yielding an iodine derivative insoluble in aqueous-acid media:

To an aqueous solution of the sample (containing not over 0.25 gram of antipyrin in about 50 cc. of water) in a 500 cc. Erlenmeyer, add 20 cc. of conc. hydrochloric acid and 50 to 60 cc. of 0.1 *N* iodine (or half the quantity of 0.2 *N* iodine), shake well and allow the tarry precipitate to settle clear by standing quietly three hours, or preferably over night, in which event 10 cc. of conc. hydrochloric acid will suffice. Decant the clear supernatant liquid through a funnel plugged and overlaid with glass wool and a little asbestos. Wash the tar 8 or 9 times by vigorous twirling of flask and subsequent decantation with 20 cc. portions of 5 per cent hydrochloric acid, keeping as much of the tar in the flask as possible. Place funnel containing the major portion of tarry precipitate in neck of a 250 to 300 cc. separatory funnel, dissolve the tar remaining in Erlenmeyer by gentle warming with about 20 cc. of methyl alcohol (free from ethyl alcohol and acetone), making sure that all the tar is in solution, then pass through the filter into the separatory funnel. Wash out the flask several times with small portions of methyl alcohol, passing each portion successively

<sup>1</sup> *J. pharm. Chim.*, 1900, I, II, 98.

<sup>2</sup> *Ber.*, 18 (1885), 1617.

<sup>3</sup> 0.008 g. iodoantipyrin is soluble in 100 cc. water at  $24.5^\circ$ . Bougault found the solubility at  $17^\circ$  to be 0.080 in 100 cc. water.

<sup>4</sup> *J. pharm. Chim.*, 6 (1912), 211.

through the filter. The washing is continued until all the tar is completely transferred to the separatory funnel, as indicated by a colorless filter. Fifty cc. or even less of methyl alcohol will usually suffice to complete the operation. Add 5 cc. of sodium bicarbonate and 50 cc. of water, then shake vigorously at intervals for a period of 5 minutes. Remove excess of iodine with a few drops of conc. solution of sodium thiosulfate and extract the iodoantipyrin with three 40 cc. portions of chloroform, washing each portion in succession in a second separatory funnel with 10 cc. of water prior to withdrawal through a small dry filter into a 100 cc. tared beaker, or, if solvent is to be regained, into a 200 cc. tared Erlenmeyer. The final operations are identical with those indicated under Method I.

make a very accurate tablet granulation and to work on this known mixture until a suitable method for assay was found. The method which was finally found to give satisfactory results, both on the granulation and the tablets, is a modification of the sulfide method, the details of which will be given later.

The first method tried consisted of the use of potassium iodide solution for dissolving the mercuric iodide and the subsequent determination of mercury in the filtrate by evaporation to dryness with nitric acid and precipitation with hydrogen sulfide, but this was found to give very low results. Some modifications of this method were also found to give low results, due to the difficulty in filtering and washing the insoluble matter free from potassium mercuric iodide, and also to loss in the evaporation to dryness with nitric acid. In precipitating with hydrogen sulfide in a hydrochloric acid solution it was necessary to wash the precipitate with carbon disulfide. As the tablets showed only a very faint trace of iron, precipitation in ammoniacal solution was later used in this method and also in the modification of this method which was found to give accurate results.

Hunter's method for the determination of small amounts of iodine was suggested and tried with results that were also low, owing to the difficulty in fusing the mixture and dissolving the fusion.

Another method was tried which consisted in the use of an acid mixture for the solution of the mercuric iodide and the subsequent precipitation with  $H_2S$  in ammoniacal solution. This gave somewhat higher results but they were not uniform.

In making the tablet granulation a formula was used containing the ingredients mentioned above, which were known to be present in the tablets in question. Of the dried granulation 4.22 grams represented one grain of mercuric iodide. This amount was taken for all of the assays on the granulation.

The method which was found to give accurate results is as follows:

Powder a sufficient number of tablets to represent 1 to 2 grains of mercuric iodide. Place in a 180 cc. Erlenmeyer flask and add 20 cc. of 1:1 HCl. Add about 0.5 gram  $KClO_3$  and stopper with a glass tube reflux condenser. Digest on the sand bath until the mercuric iodide is all dissolved. Cool and dilute with water to about 100 cc. Wash glass tube condenser and remove. Blow out chlorine with a current of air. Filter and wash insoluble matter by decantation. Make filtrate alkaline with ammonia and precipitate immediately in the cold with a slow stream of  $H_2S$ . Let stand for a few hours and filter through a weighed Gooch crucible. Wash with water and alcohol, dry at 100° C. and weigh. Grams of  $HgS \times 30.17$  = grains of  $HgI_2$ . Grams of  $HgS \times 1.955$  = grams of  $HgI_2$ .

The results of the analytical work using this method are as follows:

	Grains $HgI_2$
Tablet granulation—5 assays	1.11
(4.22 g. taken contained 1.0 grain $HgI_2$ )	1.08
	1.04
	1.12
	1.03

WEIGHT OF ANTIPYRIN TAKEN, 0.2500 GRAM

Amount of approximately N/10 iodine used Cc.	Recovery		
	As iodoanti- pyrin Gram	As antipyrin calculated Gram	Percentage
80	0.4144	0.2481	99.24
90	0.4184	0.2505	100.2
100	0.4192	0.2509	100.36
70	0.4188	0.2507	100.28
90	0.4146	0.2483	99.3
100	0.4136	0.2478	99.1
90	0.4182	0.2504	100.16
90	0.4151	0.2485	99.4
100	0.4179	0.2502	100.08
60	0.4178	0.2502	100.08
65	0.4186	0.2506	100.24
90	0.4136	0.2476	99.04
100	0.4164	0.2494	99.76
80	0.4134	0.2476	99.04
100	0.4164	0.2494	99.76
100	0.4163	0.2494	99.76
100	0.4175	0.2501	100.04

The above table represents a series of results obtained in this laboratory with an aqueous solution containing in 300 cc: antipyrin  $7\frac{1}{2}$  grams, acetanilide 1.6 grams, phenacetin 0.3 gram, sulfonal 0.8 gram. Ten cc. (equal to 0.25 gram of antipyrin) of this solution were used in each case and the method followed as described, except that the amount of iodine used was varied somewhat. This is indicated in each case in the table. The quantities of acetanilide, phenacetin, and sulfonal used were such as would make approximately saturated solutions with respect to each of these ingredients.

SYNTHETIC PRODUCTS LABORATORY, BUREAU OF CHEMISTRY  
DEPARTMENT OF AGRICULTURE, WASHINGTON

### THE DETERMINATION OF MERCURIC IODIDE IN TABLETS<sup>1</sup>

By A. W. BENDER

Received May 22, 1914

Some difficulty was experienced by the writer in finding a method for the accurate determination of mercuric iodide in tablets, and having found one that gives very good results, it was thought that it might be of some interest to others engaged in analytical work.

The work was confined chiefly to the assay of tablet triturates (compressed), and the difficulty experienced was due, in a large measure, to the other ingredients in the tablets, namely, terra alba, potato starch, talc and gelatine. Several methods and modifications of methods were tried on the tablets with very unsatisfactory results. It was then thought advisable to

<sup>1</sup> Presented at the 48th Meeting of the American Chemical Society, Rochester, New York, September 8-12, 1913.



	Grams HgI <sub>2</sub>
Powdered mercuric iodide -2 assays (0.1 gram sample).....	0.1004
	0.1024
	Grams HgI <sub>2</sub>
Tablet triturates, 1/16 grain -6 assays (sample, 30 tablets).....	0.97
	1.01
	0.97
	0.99
	0.98
	1.00

The method is simple and easy to manipulate and the results obtained were very satisfactory. It was also found to be useful for the assay of mercuric iodide and oleate of mercury.

ANALYTICAL DEPARTMENT, PARKE DAVIS & CO.  
DETROIT, MICHIGAN

## LABORATORY AND PLANT

### THE DEVELOPMENT OF THE ROTARY KILN AND ITS APPLICATION TO VARIOUS CHEMICAL AND METALLURGICAL PROCESSES<sup>1</sup>

By RICHARD K. MEADE

#### BLACK ASH REVOLVERS

As early as 1848 W. W. Pattinson, an English chemical engineer, invented a revolving black ash furnace but the furnace as he built it was not a success. It remained for Elliott and Russell some five or six years later to design a furnace which would operate successfully and this was employed in the works of the Jarrold Chemical Company, South Shields, Eng., where the practical difficulties encountered in its operation were overcome by J. C. Stephenson. The apparatus became quite popular after this and was generally introduced into alkali works both in England and elsewhere.

The black ash furnace or "revolver" (Figs. 1 and 2) consisted of a horizontal cylinder of wrought iron about 30 ft. long by 10 ft. in diameter lined with fire brick and

and the molten charge poured through the openings into cars placed below.

#### REVOLVING METALLURGICAL FURNACES

The counterpart of this furnace is found in the metallurgical industry in the Brückner ore roaster, largely used at one time in this country for calcining and desulfurizing copper ores. The Brückner roaster

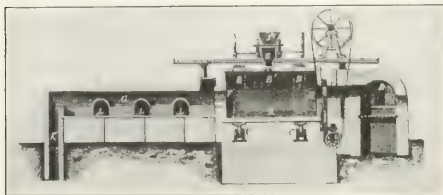


FIG. 1—SODA-ASH REVOLVER

provided with two bearing rings or tires of steel which rested upon four small flanged wheels, or rollers. The cylinder was revolved by means of a girth gear meshing with a pinion, which latter was driven by means of a small steam engine. The cylinder was provided with openings at either end, communicating with a furnace and a lye evaporator respectively. The gases from the furnace passed through the cylinder and melted the charge, the cylinder being revolved meanwhile. The waste gases passed over into the lye evaporator and the heat was utilized there. The furnace was not continuous but was operated by charging the materials (a mixture of salt cake,  $\text{Na}_2\text{SO}_4$ , limestone and coal) into the cylinder through man-holes in the side of the former, from hoppers placed above the cylinder. These openings were then closed by suitable covers and when the charge was finished the covers were removed, the furnace tilted

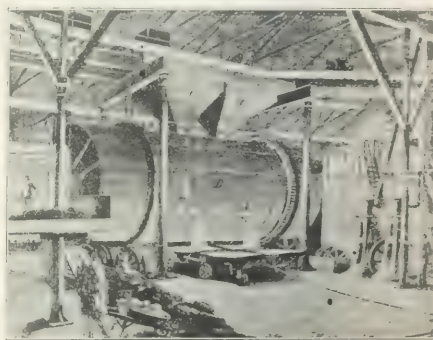


FIG. 2—SODA-ASH REVOLVER, EMPTYING THE CHARGE

does not materially differ from the soda revolver except that the evaporator flue is omitted and often the fire box is a car running along a track at right angles to the center line of the furnaces. In this way, the car can be connected with any furnace and allowed to remain there until the sulfur ignites, when it may be

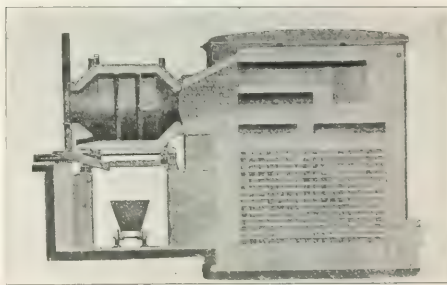


FIG. 3—SIEMENS REVOLVING STEEL FURNACE

wheeled to the next cylinder and a current of air allowed to pass through the first cylinder to burn off the sulfur.

In 1869, Siemens, the celebrated English metallurgist, applied a somewhat similar furnace (Fig. 3)

<sup>1</sup> Presented at the 6th Semi-annual Meeting of the American Institute of Chemical Engineers, Troy, N. Y., June 17-20, 1914.

to the manufacture of steel direct from the ore and Danks, of Cincinnati, Ohio, about this time invented a rotary puddling furnace which worked upon the same principle. Both the Siemens and the Danks furnace were extensively used.

Crampton, another Englishman, in 1872, took out a patent upon a rotary puddling furnace (Fig. 4). He proposed to heat his furnace, however, with powdered coal. Crampton's first furnace was used at Woolwich

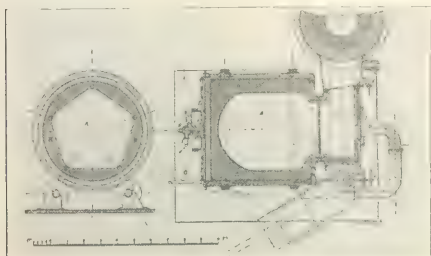


FIG. 4—CRAMPTON'S ROTARY PUDDLING FURNACE

Arsenal, in 1873, and also at other English iron works. His furnace differed from those of Siemens and Danks in that the cylinder was open at one end only, the jet of fuel and air being blown in below while the gases passed out above.

Crampton evidently understood the value of pulverized coal. It is of interest to note that this form of fuel, after nearly twenty years of successful use in the cement industry, is just beginning to be used to any extent for puddling iron, and yet Crampton suggested that it be so used over forty years ago. His furnace was designed not only to save the labor of fettling and rabbling the iron but also that of stoking the coal on the grate.

#### THE ROTARY CEMENT KILN

A few years after this, Crampton conceived the idea of using a rotary furnace heated by pulverized coal for burning cement, but, although he took out a patent in 1877 on his process, I can find no mention of his ever having put his invention into practical use.

In 1885, an English engineer, Mr. Frederick Ransome, received a patent upon a continuous rotary furnace process for burning Portland cement. Ransome's furnace differs from those which have been mentioned above in that it consisted simply of a straight cylinder, supported upon rollers and revolved by gears, tilted slightly at an angle to the horizontal. The effect of this tilting was that when material was fed into the upper end the revolutions of the cylinder caused the material to move through the furnace. As the lower end was left entirely open the action of the furnace was continuous, the material to be calcined passing in at the upper end and the burned material out at the lower in a steady stream. This is the present day "rotary kiln" (see Figs. 6 and 7).

Ransome's idea was faulty in that he expected to eliminate the necessity of grinding the burned clinker by his process rather than to effect any economy of labor or fuel in the burning process itself. His idea

was that by calcining the raw material in the form of a fine powder in such a furnace the clinker so obtained would be fine also and hence would not need to be ground. He entirely overlooked the fact that semi-fusion must take place in order to form Portland cement and that in this condition the material would be sure to stick together and form small nodules. Instead of making a clinker easier to grind the rotary kiln made a clinker much harder to grind than that burned by the upright kiln. Ransome's process was given quite a prolonged trial at a cement works at Grays, Essex, England, using gaseous fuel, but did not prove commercially successful.

In the same year, H. Mathey, of New York, took out a patent upon a revolving furnace (Fig. 5), somewhat similar to that of Ransome except that, instead

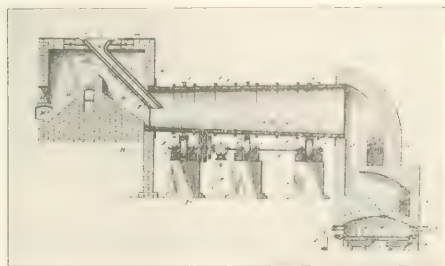


FIG. 5—MATHEY'S REVOLVING LIME AND CEMENT KILN

of inclining his furnace, he obtained the same effect by having the center line of the kiln horizontal but the kiln itself was made slightly cone shape, the material being fed in at the smaller end. He proposed to heat his kiln by a grate fire and to employ it for burning lime and hydraulic cement.

In this country, a small cement plant in Oregon attempted to use Ransome's kiln, in 1887, but the attempt here too proved a failure. About the same time the Atlas Portland Cement Company began to experiment with Ransome's kiln, first at East Kingston, New York, on wet materials and later with success upon the cement rock of the Lehigh District in Pennsylvania. In Ransome's original patent, he proposed to heat the kiln by producer gas but its development in this country was made possible by the use of crude oil. At first these kilns were only 40 ft. long, but it was soon found more economical to lengthen them to 60 feet, and now the usual length is between 100 and 150 ft. with diameters ranging from 7 to 9 feet.

The rotary kiln came quite generally into use in this country following the results obtained by the Atlas Portland Cement Company. About 1896, powdered coal in place of oil came into use and from that time on all new plants for the manufacture of Portland cement installed rotary kilns, employing pulverized coal as a fuel, except in localities where oil or natural gas are cheaper. Practically all Portland cement made in this country and much of that in England and Germany is now burned in rotary kilns.

It is not the purpose of the present paper to treat of the employment of the rotary kiln in cement burning, as the literature obtainable on the subject is voluminous, but instead to call attention to its employment in other industries and to suggest new uses to which it may be put. . .

#### DESCRIPTION OF THE ROTARY KILN

The rotary kiln (Fig. 6) in its usual form consists of a cylinder, from 6 to 9 feet in diameter by from 60 to 150 feet long, made of steel sheets from  $\frac{1}{2}$  to  $\frac{3}{16}$  inch in thickness, lined with fire brick and inclined at a pitch of from  $\frac{3}{8}$  to  $\frac{3}{4}$  inch to the foot. The steel sheets are held together with single strap butt joints, as these joints resist expansion strains due to heating better than lap joints. This cylinder is supported on two or more tires made of rolled steel, and having a face of from 6 to 12 inches and a thickness of at least 4 inches. They run each on heavy friction rollers made of cast steel, which are often mounted in pairs on a rocker. The kiln is driven by a girth gear situated usually near its middle or upper end, and a train of gears, actuated either by a line shaft or a motor. The upper end of the kiln projects into a brick flue which is surmounted by a steel stack. The flue is provided with a door at the bottom to take out the dust which accumulates there.

The lower end of the kiln is closed by a hood into which the kiln projects. Sometimes this hood is made stationary with movable fire-brick doors, but oftener it is mounted on a movable carriage. The front wall of the hood is provided with two holes, one for the entrance and support of the burning apparatus, and the other for observing the operation of the kiln and for inserting bars to break up the rings formed and

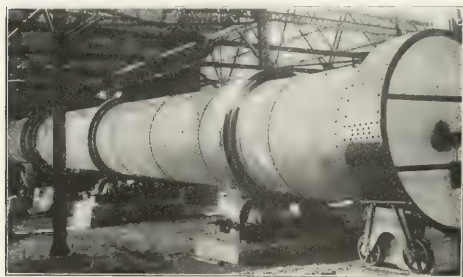


FIG. 6 ROTARY KILN

repair the lining. The lower part of the hood is partly open and through this the clinker falls. Air for combustion also enters here. Fig. 6 represents a completed kiln.

The usual diameter of a 60 foot rotary kiln unlined is from 6 to 7 feet, of a 100 foot rotary from 7 to 8 feet and a 125 foot rotary 8 to 8 $\frac{1}{2}$  feet. Most of them are made the same diameter throughout, though some of them are made, say 6 feet 6 inches in diameter for the first 30 feet and then taper through 10 feet to a diameter of 5 feet 6 inches for the remaining 20 feet; others taper for the last 10 or 15 feet before

entering the stack. This latter plan has the effect of a damper, crowding the heat more to the front of the kiln. It probably lessens the output somewhat, since the choking cuts down the amount of coal that can be burned.

The short 60 foot kilns usually bear upon two or three tires and longer kilns often on four or more tires. The kilns are always provided with two or more horizontal thrust roller bearings to keep the kiln on the vertical roller bearings.

The material to be burned is fed into the kiln through a horizontal water-jacketed screw-conveyor, or more generally spouted directly into the kiln through an inclined pipe of cast iron. Wet materials are often pumped directly into the kiln. The raw material feeding device is attached directly to the driving gear of the kiln so that when the kiln stops the feed also stops. The material to be burned is stored in large steel bins above the feeding device so that a constant and regular supply may be always at hand.

The kiln is heated by a jet of burning fuel, usually powdered coal where the ash of this is not objectionable. Where the ash of the fuel is objectionable producer gas is usually employed. Where oil or natural gas are cheaper they are always used as they are also the most convenient fuel.

#### NODULIZING ORES, CINDER, ETC.

About 1900, various metallurgists were experimenting with the rotary kiln for nodulizing flue-dust, fine iron ores, etc. Edison conducted experiments, for example, on the nodulizing of the fine concentrates obtained from his magnetic separators and several iron and steel concerns experimented with the use of the kiln to nodulize flue-dust and fine iron ores. Within a few years plants were established for the latter purpose. The Pennsylvania Steel Company were among the early users of nodulizing kilns, employing one on Cornwall concentrates. From about the year 1904 on, the patent office has issued many patents on various processes for nodulizing ores.

The rotary kiln has furnished a simple means of utilizing the soft clayey ores, such as that of the Mayari field in Cuba. Practically all of the schemes tried for placing this ore in satisfactory condition for the blast furnace were unsatisfactory until the rotary kiln was tried. The plant in Cuba now consists of twelve kilns 100 feet long (eleven of these being 10 feet and one 9 feet in diameter), and has a capacity of from 1500 to 2000 tons of nodules per 24 hours.

Chemical manufacturers also began about 1904 nodulizing pyrites cinder or "blue billy" selling the nodules to the blast furnaces. This was possible because the process not only nodulized the cinder but also desulfurized it. This practice has now become quite general and nearly all large sulfuric acid manufacturers whose locations permit of a ready sale of the product to the blast furnaces now nodulize their cinder. When copper bearing pyrites ore is roasted for the sulfuric acid and then leached for the copper, the iron oxide residue is now nodulized and sold to the blast furnaces, the wet residue being conveyed direct from the leaching tanks to the kiln.



During the past year, a great deal of interest has been aroused in the possibility of treating fine copper ores and smelter flue-dust in the rotary kiln and one of my associates, Mr. J. H. Payne, has succeeded in solving this problem. A rotary kiln installed and designed according to his specifications has now been working successfully on such material at the plant of the U. S. Metals Refining Co., Chrome, N. J., for over a year. The fine ore question is a very serious one to the copper smelter because of the fine condition of the ore resulting from concentration.

The New Jersey Zinc Co., also, have employed a rotary kiln for nodulizing fine franklinite ore. From ore containing 17.1 per cent zinc, nodules containing 20.4 per cent zinc were obtained with little or no loss of metal.

The process of nodulizing does not differ very materially from other rotary kiln processes. The main point to be watched is the regulation of the temperature and the principal difficulties encountered are the sticking of the charge to the walls of the kiln.

#### BURNING LIME

In 1885, a patent was granted to Henry Mathey of New York, on a process of making lime which consisted "in first crushing the stone to a suitable degree of fineness, then burning the crushed or pulverized stone in a revolving cylinder, whereby the particles of stone are subjected to a constant and uniform heat." In the description of his process, Mathey proposed to crush the limestone to pass a No. 4 or 6 mesh screen and to burn it in the rotary furnace which he invented and which has been described previously. Siemens also mentions the use of his rotary furnace for burning lime. I believe some experiments on burning lime in a rotary kiln were also made shortly after this at one of the cement plants in the Lehigh district and also by the California Portland Cement Co.

In 1905 or 1906, the New York Lime Co. started to burn lime at Natural Bridge, N. Y., using a 100 ft.  $\times$  6 ft. rotary kiln fired by producer gas, and shortly after this rotary lime kiln plants were built by both the Union Carbide Co. and the Aluminum Ore Co. There are now in operation quite a number of rotary kiln lime plants most of which, however, are supplying lime for chemical and metallurgical purposes for reasons given below.

An application of the rotary kiln to burning lime, of peculiar interest to the chemical industry, is the employment of the rotary kiln for burning lime from the waste carbonate of lime or "lime sludge" obtained from the manufacture of caustic soda by the action of lime on soda ash. Large quantities of this waste are produced by the paper-pulp manufacturers and also by caustic soda works. Lime-sludge is also produced by beet sugar manufacturers. The rotary kiln is now employed for burning waste lime from both industries. The rotary kiln is especially suited to burning these sludges as they can be introduced into the kiln in the form of a thin mud or "slurry."

For burning lime, producer gas is usually employed for heating the kiln but, when great purity and absence

of color are not required, pulverized coal can be used to advantage. The limestone to be burned is usually crushed to pieces of one-half inch and under, before being introduced into the kiln. The objection to the rotary kiln for lime burning is principally due to this latter fact. The lime produced is in the form of dust and small pieces, whereas for building purposes most users wish lump lime. This preference is due entirely to ignorance. Fine lime is usually the result of air slaking and, as air slaked lime is partly carbonated, it is natural that the builder should demand lime in lumps. On being supplied with rotary kiln lime, he supposes it is air slaked lime and refuses it. Such lime, however, is particularly suited to metallurgical, chemical and agricultural uses, and to hydrated lime manufacture, for all of which purposes crushing of the lime is necessary.

The advantages of the rotary kiln are its low labor cost of operating, the uniformity with which it burns if properly handled and its high fuel efficiency. The labor item of lime burning can be cut in half by operating a rotary kiln and a fuel efficiency of six tons of lime for one ton of fuel has been obtained. For this reason where lime is desired for chemical uses, for hydrate manufacture, for wood pulp plants, for fertilizer and in short, where lump lime is not necessary, the rotary kiln will make lime cheaper than any other form of kiln. The first cost of a rotary plant is, however, 50 per cent greater than that of an ordinary grate-fired vertical kiln plant of the same capacity but it is 25 per cent cheaper than a producer gas plant of like output.

One great advantage of the rotary kiln is the fact that small stone can be burned in it. It is also suited to burning stones which break up into smaller pieces and crumble on heating. Such stone cannot be burned in upright kilns because of the stopping up of the draft by the spalls.

A rotary kiln lime plant usually consists of a preliminary gyratory or jaw crusher for breaking down the big stone. This is followed by some form of break down mill or crusher to reduce the stone to pieces of  $\frac{1}{4}$  inch in diameter and under. These secondary crushers are usually of the swing hammer type. The stone goes from the crusher to a bin and from this is fed automatically and evenly into the kiln. From the kiln the lime drops into a rotary cooler where it is cooled. It is then elevated into a bin from which it is drawn for shipment as needed. At several lime plants boilers are installed at the ends of the kiln making use of the waste gases from these to generate steam.

#### ROASTING OF BAUXITE, CHEMICALS, ETC.

Rotary kilns are now employed for drying and dehydrating many ores and chemicals. In 1902, a rotary kiln was installed for the dehydrating of bauxite, and this kiln has now come quite generally into use for this purpose. Producer gas is generally employed for heating such kilns, although oil or natural gas would be the most desirable fuel where either could be employed without too great expense.

A very high grade of ferric oxide pigment is now

made in the rotary kiln by heating the residues obtained from spent pickling solutions. In this case, the salt has merely to be dehydrated, the sulfur trioxide driven off and the ferrous oxide converted to the higher oxide.

One large chemical company has a rotary kiln plant for dehydrating salts containing chemically combined water. The plant consists of four rotary kilns, each 120 ft. long and 7 ft. in diameter. Producer gas is used to heat the kilns and the exit gases from the kiln are passed through a dust collecting and washing apparatus where they are scrubbed to recover valuable dust which they carry from the kiln.

The dust problem must always be considered in rotary kiln installations and where the dust represents a loss of valuable material or is likely to constitute a nuisance to the community arrangements should be made to catch this dust. With small installations, a settling chamber and water sprays will prove satisfactory but with large installations the problem is not so simple.

The rotary kiln, fired directly by a powdered coal, oil or gas flame, is one of the most economical methods of drying and dehydrating materials known. It is extensively used for drying blast furnace slag which has been granulated by water in the cement plants of the Universal Portland Cement Co. and would offer an excellent method of drying washed phosphate rock, ore, etc., where large quantities of very wet material are to be dried.

#### MAKING BICHROMATES

Mr. J. H. Payne, by employing a highly oxidizing atmosphere in the rotary kiln has been able to produce sodium chromate using this form of furnace in place of the reverberatory furnace now generally used for this purpose, and a patent has been granted him on this process.

#### BURNING PYRITES

Ducco, an Italian chemical engineer, in 1906 suggested the use of the rotary kiln for burning pyrites for the manufacture of sulfuric acid, the pyrites being fed in at one end and the air for combustion entering at the other. His first experiments on such a furnace were made in the works of Rifredi, near Florence, where the practicability of the scheme was demonstrated. Various other acid plants in Italy also use the rotary kiln for this purpose. As employed by Ducco, the internal surface of the kiln was provided with spiral grooves to facilitate the descending movement of the ore without the production of much dust.

In this country, the Pyrite Engineering, Co., Carthage, N. Y., are exploiting a system of roasting pyrites in a rotary kiln upon which they hold patents. They have installed such a kiln at the plant of the Hinckley Fiber Co., Hinckley, N. Y. This plant, at last accounts, was working successfully, burning an ore which sometimes ran as low as 20 per cent sulfur without employing any auxiliary heat. The pyrites is being roasted just as it comes from the ground, after being crushed to  $\frac{3}{4}$  inch and down, using both lump and fines together. The lower end of the kiln is closed, a series of trap doors which work automatically allow

the cinder to fall from the kiln without the admission of too much air. When the kiln is first started, the pyrites ore is kindled by means of a jet of burning sulfur.

In view of the fact that the rotary kiln is much more simple than the ordinary mechanical rabble furnace, it is remarkable that more acid and pulp manufacturers have not given them a trial.

A novel use of the rotary kiln is in the production of sulfur trioxide. This process is in use at Höchst, at Hruschau and at Hamburg. Burnt pyrites, which has been soaked in ferrous sulfate solution, is passed into the upper end of a rotary kiln, the hot gases from the sulfur burners being admitted at the lower. The kiln (Fig. 7) is provided with shelves which pick the material up as the kiln revolves and cascade it in



FIG. 7 ROTARY TUBE FURNACE FOR MANUFACTURE OF SULFURIC ACID

a spray of fine material through the current of gas passing through the cylinder. In the upper and colder part of the tube, the sulfur dioxide gas is absorbed by the burnt pyrites. As this works its way down through the cylinder to the lower end, the heat liberates all the sulfur dioxide in the form of vapors of sulfur trioxide and sulfuric acid. The gases are freed from dust and absorbed as usual. The burnt pyrite falls into a chamber at the lower end of the kiln and is re-employed by soaking in ferrous sulfate solution obtained from the treatment of pyrites containing copper.

#### MANUFACTURE OF SULFIDES

By designing the kiln so as to cut down the amount of air entering the firing end, it is possible to procure a reducing atmosphere in the kiln so that it can be used for the reduction of sulfates to sulfides. In this case, the problem is a particularly easy one because of the low temperatures necessary in this work. Calcium and barium sulfate can both be reduced to sulfides with little trouble using a grate fire to heat the kiln. Both are now made commercially in rotary kilns. Indeed, all of the more modern plants for the manufacture of barium sulfide are equipped with rotary kilns, and a large quantity of this compound is now produced and employed in the manufacture of lithophone, blanc fixe, barium salts and in various chemical processes.

In manufacturing barium or calcium sulfide, the barytes or gypsum, as the case may be, is crushed and mixed with from 25 to 30 per cent of coarsely ground coal. The mixture is then passed through a tube mill or some other type of pulverizer where sufficient water

is usually added to make of the powdered mixture a thin mud or slurry of about the consistency of thick cream. The pulverizing is carried to the point where at least 90 per cent of the mixture will pass through a 100 mesh screen. The slurry is then fed into the kiln in a regular stream, and as it works its way through the kiln, reduction takes place. Some of the sulfide formed, however, changes to carbonate.

The product obtained usually consists of from 60 to 75 per cent water-soluble barium sulfide, 20–25 per cent acid-soluble (chiefly barium carbonate) and 5 to 20 per cent insoluble. When the ore is pure and a good reducing flame is maintained a reduction to 75 per cent of barium sulfide and only 5 per cent acid insoluble is obtainable.

The kiln is heated by a fire-box with a hand-fired grate, one man being sufficient to fire the furnace and look after the kiln. The fire-box should be designed to give a reducing flame and all joints should be tight so as to prevent excess air entering the kiln. A mechanical stoker would be the thing here. About 500–600 lbs. of coal per ton of barytes burned are required to heat the kiln and a similar quantity is mixed in with the barytes.

The red hot clinker from the kiln is usually conveyed immediately to the leaching tanks or other dissolving apparatus, where the sulfide leaches out very quickly. The insoluble is converted into barium chloride, unless it is high in barium sulfate when it is refurnaced. The barium chloride solution is purified, filtered and concentrated to the point where this salt crystallizes out. The barium sulfide solution is filtered and stored in large tanks.

A rotary kiln  $7\frac{1}{2}$  ft. in diameter and 80 ft. long, rotating once every 2 minutes, will furnace from 50 to 60 tons of barytes per 24 hours. Close supervision is necessary, however, and hence many plants operate only 10–12 hours per day. This is possible because of the low temperature employed and the ease with which the kiln may be heated up. The material furnaces easily and without complications.

#### AGRICULTURAL CHEMICALS

When phosphate rock is mixed with from 15 to 20 per cent of certain alkaline fluxes such as the sulfates, carbonates and nitrates of the alkalis, finely ground and heated in a rotary kiln to the point of incipient fusion, a sintered mass is obtained in which practically all of the phosphoric acid is present in a form soluble in ammonium citrate solution. Numerous patents have been granted covering such processes but the basic principle was made known by Baskerville in 1898 and Wiborgh obtained a patent upon essentially this process the same year. The product is analogous to Thomas slag which is highly recommended as a source of phosphoric acid for plant food.

The process is commercially possible but the low price at which sulfuric acid has been obtained as well as the fact that the demand has been greatest for a water-soluble and not a citrate-soluble phosphate and the conflicting claims of the various patentees have all tended to retard the application of the process on a large scale.

The reaction whereby the potash can be made water-soluble by ignition with calcium carbonate and ammonium chloride is familiar to all analysts, as it is the basis of the determination of this element in silicates. The proposal has been made to ignite a finely ground mixture of limestone, calcium chloride and feldspar in a rotary kiln and thereby obtain a product in which the potash is soluble. The proposition has also been advanced to make white Portland cement from a mixture of feldspar and limestone, both practically free from iron, and obtain potash as a by-product, the latter being volatilized at the high temperatures employed in the cement kiln.

The first proposition for potash does not seem to promise much because of the small percentage of potash obtainable in the product—only about 3 or 4 per cent—and its consequent low value. With the second process the problem of catching the potash presents considerable mechanical difficulty.

Both the process for rendering phosphoric acid citrate-soluble and that for obtaining a potash-bearing material from feldspar have been the subjects of extensive experiments, some of which have even gone so far as trials with a full size rotary kiln, and practically all of the large manufacturers of agricultural chemicals have looked into the subject. In view of the possibilities of both processes and the heavy and sure demand for such chemicals, these processes present an attractive problem for research.

We have a small rotary kiln 20 ft. long and 2 ft. in diameter. In this we have been able to burn from mixtures of lime, soda-ash and phosphate rock, material running as high as 26 per cent citrate-soluble  $P_2O_5$ . This experimental kiln is large enough to approach very nearly plant conditions and any results which we can obtain here should be easily obtainable in a large kiln.

#### FUTURE APPLICATIONS

In conclusion, we might say that the rotary kiln seems to us peculiarly adapted to certain chemical processes and, where it can be employed, will usually be found the most economical form of furnace, for the following reasons:

1—The rotary kiln can be operated with far less labor than other furnaces. Over upright shaft furnaces the saving amounts to from 50 to 60 per cent and over reverberatory and hearth furnaces from 50 to 75 per cent. One skilled man with the assistance of a laborer at the feed end who also attends to the oiling can easily look after two  $8 \times 125$  ft. rotary kilns.

2—The upkeep of the rotary kiln is less than that of any mechanical furnace. The lining of course on some materials is subject to destruction from the scorifying action of the charge, but outside of this the repairs and renewals amount to almost nothing. Mechanical repairs on an average amount to \$2.00 per day for an  $8 \times 125$  ft. kiln. There are no rabble arms to break and no metal parts are subject to corrosive gases.

3—The power required to drive the kiln is much



less than that needed for any mechanical furnace of similar capacity. The power required for the above size kiln amounts to about 20 H. P.

4—Its continuous action promotes fuel economy and large outputs per unit. No time or fuel is lost in heating up and cooling down the kiln as with intermittent furnaces and the steady flame of the jet of burning powdered coal gives a much more uniform temperature than is possible with furnaces which are fired by hand and hence into which cold air is continuously entering when the fire is stoked. The fuel saving of the rotary kiln over a reverberatory furnace amounts to from 30–50 per cent.

5—Wet materials may be furnaced as well as dry, the upper part of the kiln acting as a drier, and both fine material and lumps may be burned at the same time.

6—The charge is at all times under control and is advanced regularly through the kiln at the desired rate. This rate may be changed at will by quickening or retarding the speed at which the kiln revolves.

7—High temperatures may be obtained and any fuel desired employed. Both oxidizing and reducing flames may be secured.

As to processes to which the rotary kiln is most applicable, these would seem to us to be:

1—Processes in which carbon dioxide, combined water or other volatile constituents are to be driven off by heat and at temperatures below 2700° F.

2—The oxidation of ores, chemicals, etc., whether this is accompanied by burning of sulfur or other combustible elements or not.

3—The reduction of compounds where this can be accomplished by heat in a reducing atmosphere either with or without the use of a reducing agent. The kiln is particularly suited to reducing processes where these consist in mixing a reducing agent with the compound to be reduced and the mixture finely ground and furnaced.

4—Processes which consist in the formation of new compounds by partially fusing or sintering a mixture of two or more materials.

5—Processes which are designed to merely change the physical state of a substance by just heating the material (either alone when fusible or with some fusible binder when not itself fusible) to the point when the particles cohere to form nodules or clinker of the desired size.

Two or more of the above processes are often carried out in the same furnace, as for example in the manufacture of Portland cement, where the carbon dioxide is first driven off and then the silicates and aluminates of lime are formed.

The rotary kiln is not suited to reactions which are attended with marked fusion of the material, that is, when the mass must become fluid before or in order for the reaction to take place. When the fusion takes place above the temperature at which the reaction is completed, the rotary kiln may be employed with

proper care to control the temperature. Where only sintering takes place the kiln, of course, gives entire satisfaction and many reactions which ordinarily require fusion of the mass to take place may be carried out completely without having the mass either molten or even pasty, by simply grinding the components finely and heating only to the point of incipient fusion or sintering. Here the greater surface exposed allows the reaction to take place by diffusion. Examples of this are found in the process of making available phosphoric acid referred to above and also in the burning of cement clinker.

202 NORTH CALVERT ST.  
BALTIMORE

## A COMBINATION WATER SOFTENER AND STORAGE TANK<sup>1</sup>

By L. M. BOUTH

Any water purification process implies that the purified water is to be used. How best to store this water between the time it is purified and used is a matter for consideration. In some industrial plants, the rate of use of water is fairly constant throughout the day, the water is used as fast as it is softened and no storage is necessary. Most water users, however, have one or more considerable peaks in their load requiring the delivery of large volumes of purified water during a short space of time. The usual plan has been to provide a separate tank or reservoir.

During the past ten years a great many softeners equipped with excelsior filters, affording storage capacity for one hour's flow (more or less)—sufficient for ordinary requirements of an industrial or power plant—have been built. Usually, this storage capacity is provided by increasing the height of the tanks a few feet above the filter to gain the desired volume. A softener arranged to include storage capacity above the filter is shown in Fig. 1.

This provision for storage capacity, while adequate to serve the needs of most power plants, necessitates the use of raw water for, perhaps, half a day, twice each year, in order to provide opportunity to change the filtering material. To use raw water, pumped directly to the feed water heater for boiler feed, for such a brief interval, is not especially objectionable. For railway water stations, however, such a plan has very little to commend it, because during the periods of filter cleaning, there would be no water available, stored at sufficient height, to fill a locomotive tender in the usual short period.

The best water softening practice in vogue at the time the first modern water softeners were imported from Europe, late in the nineteenth century, called for the use of filters to clarify the imperfectly settled water. Usually, these filters were constructed of "excelsior" (wood shavings). Careful observations of softeners operated at a small fraction of the rated capacity—corresponding to more liberal design—readily demonstrated that if the rate of upflow in the settling space were restricted to a very slow flow,

<sup>1</sup> Presented at the 6th Semi-annual Meeting of the American Institute of Chemical Engineers, Troy, N. Y., June 17–20, 1914.

practically no suspended matter reached the filter. By gradually adopting more liberal standards of settling

feature of water softener construction, it becomes a simple problem to add any reasonable amount of pure water storage.

As a result of several years practical experience and study, having in mind the possible elimination of

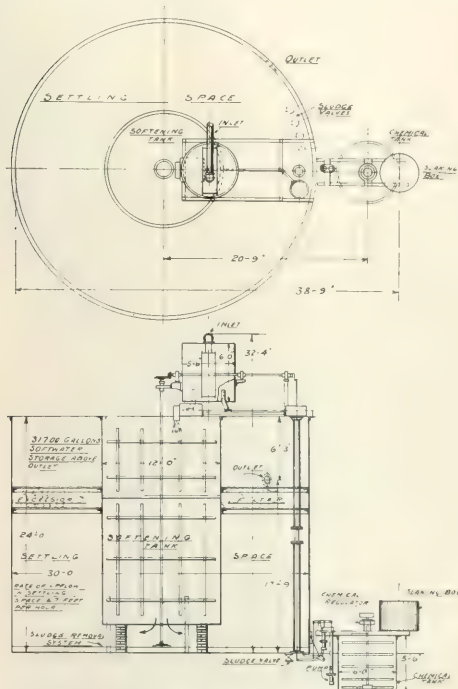


FIG. I—WATER SOFTENER—CAPACITY 30,000 GALLONS PER HR.  
Dayton Power and Light Co., Dayton, Ohio

tank design, the point is soon reached when the expense of installing and maintaining a filter for purifying boiler feed water is not justified.

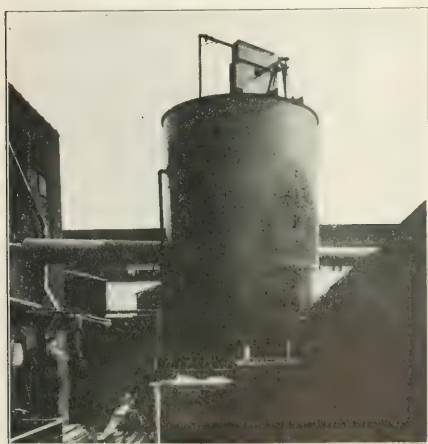


FIG. II—WATER SOFTENER—CAPACITY 5,000 GALLONS PER HR.  
National Malleable Castings Co., Toledo, Ohio

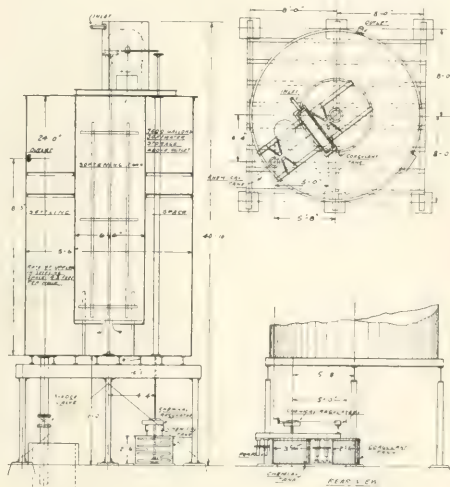


FIG. III—WATER SOFTENER—CAPACITY 5,000 GALLONS PER HR.  
National Malleable Castings Co., Toledo, Ohio

the filter, the softener at the foundry of the National Malleable Castings Company, Toledo, Ohio, as shown in Figs. II and III, was designed and installed to soften



FIG. IV—WATER SOFTENER—CAPACITY 50,000 GALLONS PER HR.  
Chicago, Rock Island and Pacific Railway, Burr Oak, Ill.

and clarify hard and sewage laden muddy Maumee River water for boiler feed.

More rapid progress toward the development of the "No-Filter" softener for purifying boiler feed water would have been possible except for the popular preju-

After demonstrating that the filter is not an essential

dice favoring the use of a filter of some kind. The average individual cannot conceive how it would be possible to simplify and improve a softener by omitting the filter. Several of these "No-Filter" installations having been made, and having demonstrated their fitness to meet the requirements, the construction of a "No-Filter" softener equipped to store purified water, has become a commercial proposition. A typical installation of this kind is shown in Fig. IV.

Somewhat more than the upper half of this tank, which is 40 feet high, is devoted to the storage of softened water. Fig. V shows the general arrangement of this softener.

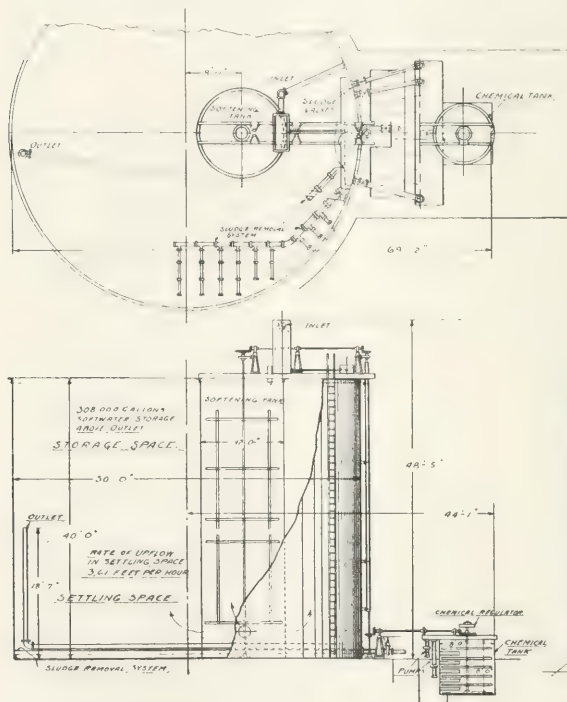


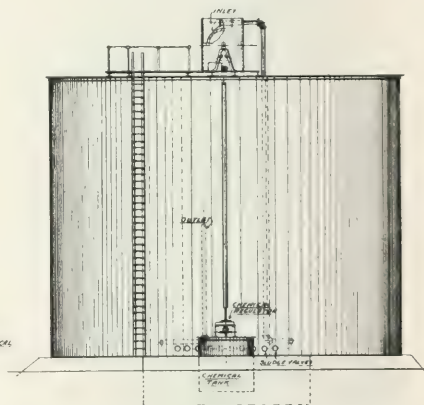
FIG. V - WATER SOFTENER  
CAPACITY 50,000 GALLONS PER HR  
Chicago, Rock Island and Pacific  
Railway, Burr Oak, Ill.

than the rated capacity of 50,000 gallons per hour, the time of flow is proportionately longer.

The action of the softening tank mechanical agitators in preparing the precipitate for sedimentation is described below and is shown in Figs. VII and VIII.

From the softening tank the water flows upward through the settling space at a rate of 3.61 feet per hour, which is sufficiently slow to effect clarification of this particular water. The time of flow from the bottom of the softening tank to the outlet corresponds to 4.4 hours when the softener is operated at rated capacity.

There is available for immediate use 308,000 gallons of softened water above the outlet. This volume is



The water enters at the inlet and passes to an overshoot waterwheel which furnishes the power to drive the agitator in the softening tank, as well as the agitator in the chemical tank at ground level. This same power also operates the chemical feed pumps. One of these pumps delivers the chemical solution to the chemical regulator located on the chemical tank, and the other elevates the solution which has been measured by the chemical regulator, to the top of the softening tank, where it meets the raw water which has passed over the waterwheel.

The downflowing water and chemicals are thoroughly mixed in this softening tank, during a period of twenty-eight to forty-eight minutes, depending on the amount of water in the storage space. When operated at less

sufficient to meet the demands of a large locomotive terminal and freight yard.

Fig. VI shows in detail the manner of handling the chemical solution. The reagents used are hydrated lime and soda ash.

The low lift pump takes its suction through a strainer screen near the bottom of the chemical solution tank. The solution is delivered to the inlet compartment of the chemical regulator, mounted on the chemical tank. The level of the solution in this compartment is maintained at constant height, for the reason that sufficient solution is delivered into it to keep the solution continually overflowing the inner weir. The excess solution returns to the chemical tank. A uniform flow of solution, sufficient to treat 50,000



gallons of water per hour, from the inlet compartment flows through the standard orifices, which are always under a constant head. When the softener is run at full capacity, all of this solution is required; but if, for instance, it is operating at one-half capacity, as shown in the detail view of the chemical regulator, only one-half of the maximum flow of solution passes down the feed chute to the high lift pump, by means of which it is delivered to the softening tank. The other fifty per cent, which passes the cut-off plate on the other side, returns directly to the chemical tank. Similarly the feed is directly proportional to the amount of water entering the softener for all other rates of flow. The chemical regulator cut-off plate is actuated

the chemical regulator and thus control the proportional feeding of the chemical solution.

Aside from a liberal design of settling tanks, there is one other important feature of this type of softener which materially assists the settling tank to deliver a clear water. This is the provision for mechanical agitation in the softening tank. The agitation is continued sufficiently long not only to thoroughly distribute and mix the chemicals with the water but also to insure coagulation of the precipitate, so that it will settle promptly as soon as the quiet condition of the settling tank is met.

Fig. VII is an example of the influence of mechanical agitation as compared with another softening experi-

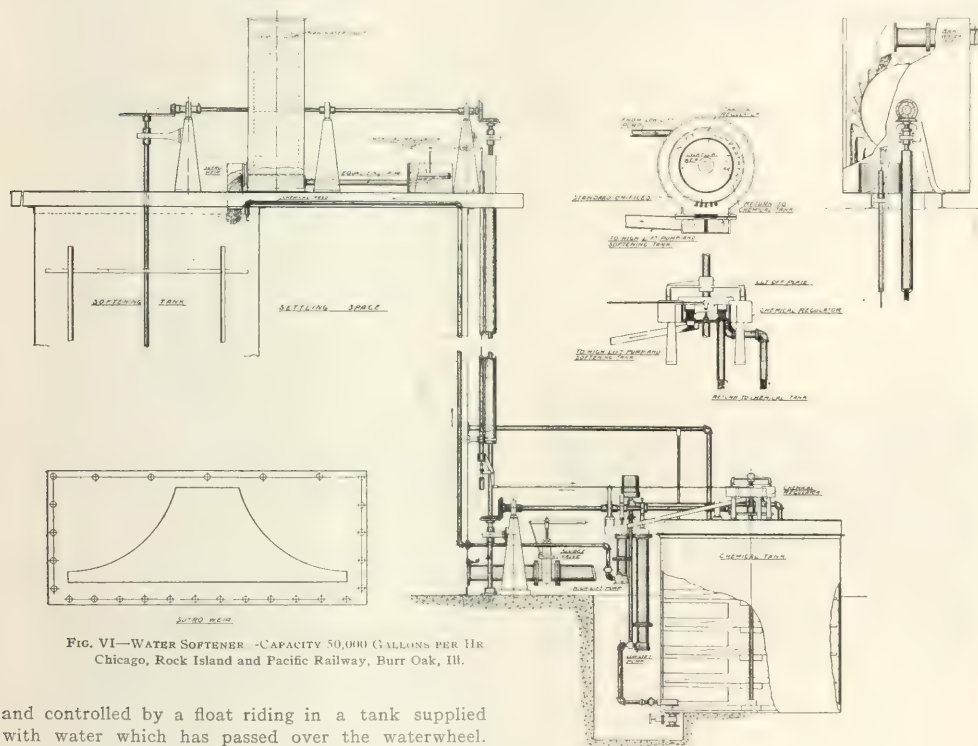


FIG. VI—WATER SOFTENER—CAPACITY 50,000 GALLONS PER HR  
Chicago, Rock Island and Pacific Railway, Burr Oak, Ill.

and controlled by a float riding in a tank supplied with water which has passed over the waterwheel. The varying heights of water in the lower part of the wheel box are transmitted to the float tank through an equalizing pipe.

The outlet for the hard water from the wheel box, into the softening tank is through a Sutro weir, the general shape of which is shown in the detailed view. The extreme width of this weir opening is 25 inches. In view of the fact that the height of the water flowing through the Sutro weir is at all times directly proportional to the quantity, it will be seen that the vertical movements of the regulating float are always proportional to the quantity of water flowing. The vertical movements of this float are transmitted by means of a lever, links, and bell crank to the cut-off plate of

ment similar in all respects, with the exception that only a slight mixing was given in VII-b, the "unstirred," whereas, VII-a had been subjected to the kind of agitation which experience has shown to be the most sufficient for precipitates of this kind.

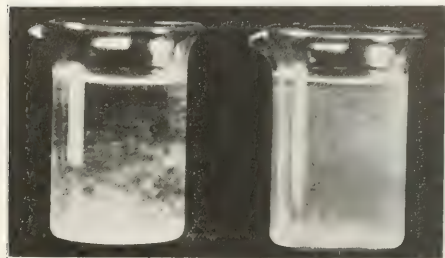
The photograph (Fig. VII) was taken at the end of three minutes following the addition of chemicals at the rate of 1.9 lbs. of lime and 1.2 lbs. of soda ash per thousand gallons. The raw water in this case had a hardness of 285, and an alkalinity of 235 parts per million, corresponding in grains per U. S. gallon to 16.6 and 13.7, respectively.

In the experiment with Sample *b* there was only

a slight mixing of the water caused by eight revolutions of the agitator whereas Sample *a* was stirred for three minutes, at the end of which time the precipitate

is stored at a considerable elevation suitable for delivery, without pumping, to feed water heater or locomotive tender.

136 LIBERTY STREET, NEW YORK



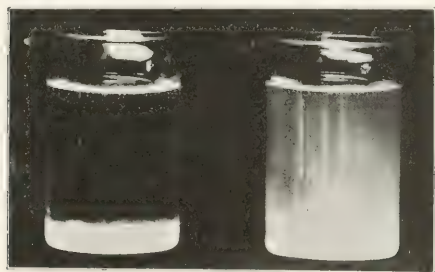
a - Stirred. b - Unstirred

FIG. VII - WATER SOFTENING EXPERIMENTS AT END OF 3 MINUTES

had become fairly well coagulated. The slight blur in Sample *a* shows that while the stirring had ceased, the precipitate had not yet come to rest.

Fig. VIII shows the same samples, neither of which has been touched since the first photograph was taken. The second photograph shows the difference at the end of six minutes, by which time the precipitate in Sample *a* had almost completely settled, whereas Sample *b*, as may be noted, shows its precipitate to be very much behind in development.

These simple experiments demonstrate clearly the advantage gained by the proper kind of mechanical agitation while the precipitate is in process of formation.



a - Stirred b - Unstirred

FIG. VIII - WATER SOFTENING EXPERIMENTS AT END OF 6 MINUTES

As already stated, the use of mechanical agitation plays an important rôle in the "No-Filter" softener, which makes feasible the storage of a large volume of softened water in the same unit with the softener.

Some of the advantages of this softener are:

1—All handling and regulation of chemicals is accomplished at ground level.

2—Mechanical agitation for the softening tank is provided.

3—There is sufficiently slow upward flow in the settling space to deliver a clear effluent.

4—Convenient arrangement of storage capacity.

The combination of the softening and storage features results in a saving of ground space as well as in cost of the plant. No separate foundation is necessary. It is an important advantage that the water

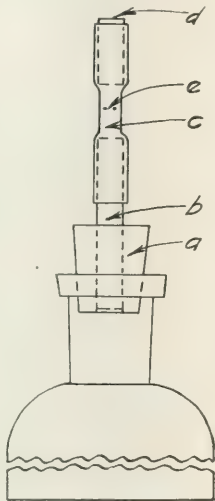
## A NEW SEAL FOR THE PREVENTION OF AERATION IN DEAERATED LIQUIDS

By FRANK BACHMANN<sup>1</sup>

Received August 3, 1914

There have been several devices recommended for preventing the absorption of atmospheric oxygen in the methylene blue test for putrescibility. Among the devices recommended are: Jackson's bulb pipette<sup>2</sup> and Buswell's capillary U-tube.<sup>3</sup>

The Bunsen valve shown in the figure has given very satisfactory results at the Sewage Testing Station of the Sanitary District of Chicago. The valve consists of: a rubber stopper "a," through which a glass tube, "b," passes; rubber tube "c" is attached to the upper end of the glass tube and closed with a glass rod, "d." Ordinarily, a slit is used in the rubber tubing, but in this case a few pinholes were punched in the tubing as shown at "e." The pinholes open and allow the gases to escape but close by pressure from without and thereby prevent the ingress of air. The bottle is filled with the liquid under examination and the rubber stopper with valve forced in place. The liquid rises in the glass and rubber tubing, thereby displacing practically all of the air in the tube.



To show that the Bunsen valve prevents re-aeration, water-sewage mixtures were prepared and placed in bottles with methylene blue, using cork, glass and Bunsen valve seal as stoppers and then incubated at 37° C. The temperatures of the mixtures before placing them in the incubator were about 19° C. In the case of the cork and glass, the stoppers loosened to allow some liquid to escape, due to the expansion of the liquid. The Bunsen valve cared for this expansion very satisfactorily. After the liquids decolorized, the bottles were taken out of the incubator and gradually cooled. Reabsorption took place rapidly in the bottles stoppered with glass and cork, as shown by the reappearance of the methylene blue, whereas practically no blue appeared in the Bunsen valved bottle. The rubber tube on the Bunsen valve collapsed, thus preventing the absorption of air by the liquid.

In a series of tests with methylene blue and a putres-

<sup>1</sup> Assistant Chemist, The Sanitary District of Chicago.

<sup>2</sup> Jackson and Horton, *This Journal*, 1 (1909), 328.

<sup>3</sup> Buswell, *Ibid.*, 6 (1914), 325.

cible mixture using cork, glass and Bunsen valves as stoppers for comparison, and incubating at both 20° C. and 37° C., it was found that there was practically no difference in the relative stabilities of each mixture incubated at the same temperature. The mixtures were at about 18° C. when placed in the incubators, thereby giving the stoppers an opportunity to loosen with the expansion of the liquid and consequently to absorb oxygen from the air. Judging from the results of the relative stabilities, no oxygen was absorbed. The question of the importance of oxygen absorption from the air in incubation tests has, to my mind, been more or less exaggerated. If the liquid is brought to the incubation temperature and a good grade of cork or glass stopper inserted into the bottle, I do not believe that there is much danger

from re-aeration. However, to meet this slight danger, the Bunsen valve is desirable.

It may also prove valuable in the English test for the determination of the oxygen demand, where after several days' incubation a slight rise in dissolved oxygen is often noted. The seal has been of service when using Lederer's nitrate method<sup>1</sup> on domestic sewage and a particularly strong trade waste such as is met with at Packingtown. With such a strong waste, cork and glass stoppers are frequently blown out of the bottle, due to the pressure of the gases formed.

The main advantages claimed for this seal are its simple construction and simple application.

THE SANITARY DISTRICT OF CHICAGO  
39TH STREET AND LAKE FRONT

## ADDRESSES

### SHODDY AND CARBONIZED WASTE<sup>1</sup>

BY LOUIS JOSEPH MATOS

For many years there has existed a small though important industry that is devoted entirely to the working up of rags of all kinds, and of woolen waste, recovering from it the wool fiber and putting it in condition so that it can be re-used to advantage. This is the "shoddy" industry, and though somewhat prosaic, and out of the usual order of technical papers of interest to the Institute, is in a great measure dependent for its progress upon the combined skill of both engineers and chemists.

There have been proposed from time to time numerous processes for the destruction and removal of vegetable particles from wool in all stages of manufacture. Burrs, seeds and other plant fragments are found normally in most all raw wools. Fine particles of cotton or other threads occasionally, though accidentally, are picked up during the travels of pure wool through the mill; these show distinctly in piece-dyed goods when finished and call for the process of "speck dyeing" and in the better grade fabrics for "carbonizing in the piece," and finally the process of rag carbonizing which forms the basis of this paper.

The importance of this industry may be appreciated when it is realized that if all the wool clipped during any one year be converted into cloth suitable for garments and equally distributed among the inhabitants of the temperate or wool wearing zones, there would be but fourteen (14) ounces of cloth to each individual, sufficient to make only a single pair of knee breeches per person. Consequently, in order to provide a sufficient supply, wool must be obtained from another source, and this source is, of necessity, previously made and used woolen cloth in the form of rags.

The various kinds of stock that serve as raw material for the manufacture of shoddy and similar products are subject to several classifications based upon whether the rags are "new," that is, rags and clippings obtained from clothing manufacturing establishments, etc.; "old stock" or rags obtained from previously worn clothing; and "wool waste" which, as its name indicates, may be regarded as the waste sweepings from woolen mills. These groups are classified about as follows:

**NEW—CLIPS.** Clips, factory wool, fine mixed, fine merchants tailor, coarse gray, ordinary light, fine dark. *Worsteds:* choice light, fine gray, fine dark, black blue, brown. *Serges:* brown, blue, black, light, dark, light fancies, dark fancies. *Worsted edges:* blue, black. *Flannels:* new blue, new scarlet. *Plain*

*black kerseys.* *Unions:* new, dark, ordinary. *Mixed cloakings.*

**OLD STOCK**—Soft *woolens*, best, coarse. Red *flannels:* white softs. *Merinos:* fine light, fine dark, coarse dark, fine black, soft *woolens.* *Old blue flannels:* tibets; *serge*, black, brown, green, small skirted, blue skirted. *Knit stock*, white, light gray underwear, coarse gray, steel gray. *Cloth*, rough, tan, fine brown, coarse brown, skirted, small, dark, black, light blue, mixed. *Worsted*, light, blue, black, dark. *Carpet.* Soft *flannel.* *Satinet garments*, mixed *satinets.* *Seams*, mixed, *delaine*, skirted.

**WOOL WASTE**—Colors, strictly all wool *delaine*, extract, dark, light, black, blue, brown and fancy colors. Black *serge*, blue *serge.* Ring waste, fine foreign, fine domestic, coarse foreign, domestic. *Noils*, fine 1/2 blood, 3/8 blood, 1/4 blood, French combed; *carpet.* Hard ends, white *worsted*, colored *worsted.* Yarn waste, colored (all wool) *woolen*, white (*woolen*), colored (*woolen*), colored (cotton mixed), white *carpet.* Card waste, 1/4 blood, 3/8 blood, white *woolen*, colored. Burr waste, white, colored. *Pill stock*, white.

The operations necessary to convert apparently useless rags into a merchantable and useful fiber, requires that they be subjected to the action of disintegrating machines termed pickers and garnets, which pull the rags apart and break them up more by a tearing and shredding operation than by cutting, followed by a succession of garnet machines of increasing fineness whereby the threads that composed the original rags are unravelled into their constituent fibers. Under the broad term "regenerated wool" is to be included all those forms of wool that have been recovered from rags and cloth clippings.

When this disintegrating operation is carried out with soft rags or rags of unfilled woolen fabrics such as knit-goods, flannels, shawls, etc., and the waste incident to their manufacture, the result is termed "shoddy," the fibers being relatively long, averaging from 2/5 to 1 1/4 inches. On the other hand, where the rags are from originally heavily filled woolen fabrics or other classes of hard rags, the resulting fiber is termed "mungo," conveying the impression that the stock is short, due to the breaking of the fiber during the disintegrating. The length of "mungo" fiber varies from 1/5 to 3/4 of an inch. It is rarely used alone for yarns, but generally with new wool or cotton. It is further distinguished by being incapable of fulling. Extract wool, or commonly, "extract" is a regenerated wool fiber that has been freed from vegetable matters.

As is apparent, there must be present in the rags at times, certain varying amounts of cotton threads or admixed cotton,

<sup>1</sup> Presented at the 6th Semi-annual Meeting of the American Institute of Chemical Engineers, Troy, New York, June 17-20, 1914.

<sup>1</sup> Lederer, *J. Infect. Dis.*, 14 (1914), 482.

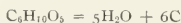


the former due to the stitching of seams, etc., while the latter is due to cotton in the cloth in the form of warp threads or loose cotton mixed with wool to make the so-called "merino" yarn. Consequently, in the "manufacture" of regenerated wool, it is necessary to make use of some chemical process that will destroy the cotton present in the rags without appreciable chemical action on the wool. This process is called "carbonizing" and the regenerated wool fiber obtained is called "carbonized stock" or "extract."

The carbonizing process dates from 1851, and is the reverse of the well-known reaction of caustic alkali on mixtures of wool and cotton, whereby the wool is dissolved leaving the cotton intact. It is recorded that a certain Captain Corbett, visiting the London Exposition in 1851, was attracted by the caustic boiling process as applied to treating cotton rags for the purpose of freeing them of wool fibers, thereby fitting them better for the use of the paper maker. However, he regarded wool as being the more valuable fiber to recover, and devised the process of treating woolen rags with weak acid to destroy the cotton. He started an extract plant at Mitcham, in Surry, but his output attracted little attention in Yorkshire, as the local makers of woollens realized at once that the fibers would not "felt" or "full" properly as they had lost their milling qualities.

Notwithstanding the work of Corbett, it is a fact that Kober, a German, and Isard and Leloup, Frenchmen, publicly used the acid carbonizing process about 1854 in their respective countries since which time there have been introduced by various inventors between thirty and forty modifications involving chiefly mechanical appliances, and it is curious to note that all the methods actually referred to in these modifications have been based upon the use of an acid reaction.

The chemical reaction forming the basis of the carbonizing process is very simple, and is as follows:



The chief results aimed at by the shoddy carbonizer are governed by the following conditions, based upon many trials made with cotton in the presence of wool and under varying conditions. At 140° to 145° F. the cotton becomes brittle and it is in this condition that the shoddy maker desires to have it. When the temperature is maintained at about 145° F. there is little or no danger of the acid injuring the wool. Between 150 and 160° F. the cotton fiber browns distinctly, but an incipient injury is done to the wool. Between 165° and 170° F. the cotton is actually charred. Therefore, using acid of from 2 to 3 per cent strength, and baking at a temperature of 140° F. the cotton is converted to a condition easily removable in the willowing machine without any action on the wool.

The most commonly employed process for rag treatment consists of immersing the rags in huge tanks containing a weak solution of sulfuric acid, generally ranging in strength from 2 to 4 per cent. After soaking for several hours, the rags are removed from the tank and drained, and the excess of acid is removed by means of a centrifugal, and returned to the tank for further use. The rags are then put through a drying oven and baked, keeping the temperature about 145° F. so that the cotton or other vegetable fiber present is completely destroyed. As many of the rags subjected to this process are previously dyed, the action of the combined acid and high temperature is in some instances likely to affect the colors, which causes the resulting "shoddy" to fall into its own particular commercial class as to colors. On the other hand, the manufacturer of shoddy and extracts is often called upon by the woolen manufacturer to supply a particular grade of shoddy dyed a special shade and to possess certain properties, such for instance as fastness to severe milling, and in consequence, the shoddy dyer must use the same kind of dyes that the dyer of the pure scoured wool must employ when equally high standards are set.

In cases where the color on the original rags is not suitable,

the shoddy manufacturer must remove or reduce it to such a point that they can be re-dyed to match the given shade. This color-removal process is called "stripping," and is accomplished by means of: (1) soda; (2) bichromate of potash, sulfuric acid and oxalic acid; or (3) with hyraldite for stripping—a zinc-formic-sulfite compound—which chemically destroys many of the dyes used for wool. These several processes are used according to the nature of the original dye on the rags.

**STRIPPING WITH SODA**—The rags are treated for not less than half an hour at 120° F. with a solution of 5 to 10 per cent of soda ash, calculated on the weight of the rags, and followed by a good rinse. Soda stripping is usually adopted for colored rags, fragments of women's dresses, etc., as they are dyed chiefly with acid colors.

**STRIPPING WITH BICHROMATE OF POTASH, SULFURIC ACID, AND OXALIC ACID**—All material that is not sufficiently stripped by the first process should be subjected to this process. Indigo and wood colors especially are stripped by this treatment, and alizarine colors are sometimes converted into shades that are more easily over-dyed. The rags are boiled for 1/2 to 3/4 hour with 3 to 6 per cent of bichromate of potash, 6 to 12 per cent sulfuric acid, and 3 to 6 per cent of oxalic acid. They are then rinsed and carbonized.

**STRIPPING WITH HYRALDITE**—Hyraldite is now largely used in the stripping of shoddy. It does not affect the fiber in the least. It destroys most acid colors as well as a great many chrome colors, so that very light-colored goods may be produced from very dark or even black material. Stock stripped with hyraldite does not have a tendency to turn a yellowish tint afterwards, as is usual with other stripping methods; this is an advantage when subsequently dyeing shades of blue, violet, green and other light mode shades. The stripping is done at a temperature of 120° F. with from 2 to 4 per cent of hyraldite for stripping, 2 1/2 to 5 1/2 per cent of formic acid, afterwards raising to the boil, and working for 1/2 hour, followed by a rinse.

Another carbonizing process that is largely used, is based upon the destructive action of gaseous hydrochloric acid generated either by allowing the liquid acid to flow slowly into an externally heated iron chamber, or by heating a mixture of rock salt and sulfuric acid. The hydrochloric acid or dry gas process in several modifications has been patented by a number of inventors, the two most important patents being issued to Messrs. Jourdin & Balan, in 1877, and the other to an inventor named Michel, in the same year.

Nitric acid in gaseous form has also been used, the gas being generated by the action of sulfuric acid upon nitrate of soda, but the result was not a success; while the cotton or other vegetable matter was destroyed, the wool fiber was considerably injured.

Certain metallic salts have been recommended from time to time, but those most commonly used have been chloride of aluminum and chloride of magnesium. The former is usually employed in solution of a strength between 9° and 10° Tw. The material to be treated is saturated by soaking for a few hours, afterwards whizzed and dried at a moderate temperature, and finally baked in the carbonizing oven at 194° F. for an hour. Usually the vegetable matter becomes very brittle and easily dusted out before this temperature is reached. Afterwards the stock is well washed. This process is less injurious to the wool than the acid process, but it is more costly. It is believed by the writer to be properly credited to Joly, of Elbeuf, France, who referred to its use particularly in carbonizing fabrics. Magnesium chloride, while destroying vegetable matter, is not as easy to handle as aluminum chloride.

There are other processes for carbonizing rags, which may be mentioned as follows: Calcium chloride in solution, recommended by Poulin, of Paris, in 1881, who used 4 parts of a solu-

tion of the calcium salt at 32° Tw. diluted with 3 parts of water. Another solution consists of 2 parts of sodium chloride and 2 parts of hydrochloric acid in 10 parts of water. Both of these solutions destroy cotton fiber, but offer no advantages over the usual processes. Since the extended use of silk for sewing and for fancy effect stripes, etc., as in the manufacture of men's and women's goods, there are immense quantities of shoddy on the market that are unavailable on account of the particles that cannot be successfully removed by any practical carbonizing process. It is a fact that silk is dissolved in a solution of ammonium-copper-oxide (Schweitzer's reagent) and without action on the wool, but while excellent results are obtained by treating small batches of shoddy with this reagent, difficulties are met that prevent its use on a commercial scale.

The handling of rags on an industrial scale has remained a thoroughly organized business, which, in the metropolitan centers is more completely specialized than in the smaller places but the operations generally work out in the following order:

- |                            |                                |
|----------------------------|--------------------------------|
| 1—Rag gatherer, or rag man | 4—Rag sorter, or shoddy dealer |
| 2—Local rag dealer         | 5—Shoddy manufacturer          |
| 3—Central rag dealer       | 6—Woolen mill                  |

A mill for the utilization of shoddy, or its conversion into finished fabrics does not differ materially from an ordinary woolen mill; the sequence of operations being in the following order, and as described, contemplate the plant commencing its operations with sorted rags as bought from the rag dealer:

- 1—Rag shaking: object—the removal of dirt, dust, etc.
- 2—Extracting or carbonizing
- 3—Stripping according to the nature of the rag: object—the removal of the old dye. This operation is sometimes omitted where the original color of the rags will serve as such in the cloth contemplated
- 4—Dyeing
- 5—Drying and oiling
- 6—Garnetting
- 7—Blending and oiling
- 8—Teasing
- 9—Carding
- 10—Spinning
- 11—Weaving
- 12—Scouring, to remove the added oils

For some classes of cloth the fabric is dyed after scouring, and when this is done, the dyeing operation No. 4, above, is omitted.

- 13—Raising and milling
- 14 Finishing

The shoddy of commerce is graded as follows: Fine white wool yarn, worsted yarn. Garnetted white shoddy, all wool. Medium white knit shoddy, all wool. New fine black worsted shoddy; medium black worsted shoddy; new blue worsted shoddy, best fine. Dark mixed yarn shoddies, extra fine and free from cotton; light yarn shoddy, extra fine; light yarn worsted; dark mixed; fine thibet, all wool; fine dark merino, No. 1 all wool. Medium dark merino, all wool; coarse dark merino, all wool; fine light merino. Coarse light merino. Medium light not all wool. Red knit shoddy, all wool. Dark blue shoddy for hosiery manufacturers, strictly all wool; and the same not all wool.

From the above it is seen that certain gradings depend upon colors and in a large number of instances, the color of the finished shoddy is that of the rags from which it is made.

The dyeing of shoddy rags to meet special demands of mills, is almost invariably done after stripping and carbonizing, since the small amount of acid remaining in the carbonized rags and not washed out aids in the dyeing.

Rag dyeing is done in either a very crude or in a most advanced way. It is either done in hugh dye-tubs where the rags are poled about by hand, or else in pressure dyeing machines where the rags are packed in fixed dye chambers and the dye liquor made to circulate through the fixed mass.

Certain of these dyeing machines have been constructed of immense size so as to handle a large quantity of rags at one time which is quite necessary owing to the average low intrinsic value of the material. Such dyeing machines have been built with double cages, one in service with a charge of 1000 pounds of rags, while the other cage is being emptied and refilled. One

such machine is sufficient to keep a fair sized shoddy mill constantly supplied with dyed rags. It is usual, however, to have one or two supplementary machines of smaller size either in reserve, or for taking care of special small dyeings.

Other types of rag dyeing machines are constructed on the horizontal revolving perforated cylinder form, in a fixed volume of dye liquor. In either case the result is practically the same.

Woolen rags—or extracted rags, that have been stripped and are to be dyed, must be so dyed as to stand the usual milling treatment that is given to the cloth of which it forms a part. Few cloths are made wholly of shoddy: varying percentages of new wool must always be used, or great difficulty will be experienced in spinning the threads.

For the production of dyeings very fast to milling the anthracene colors are used in the first place, and some acid colors which are especially fast to milling, such as milling yellow, milling red, wool red, formyl violet, formyl blue, brilliant milling blue, tetra cyanole A, alphanol blue, brilliant milling green, anthracite black and alphanol black. Numerous diamine colors are also entirely fast to milling next to wool; and some of this group, as for instance diamine fast red F, diamine green G, diamine brown R, M and B, diamine catechine G and 3 G, diamine fast gray B N, may, by an after-treatment with bi-chrome or chromium fluoride, be fixed so completely as to possess very good fastness to milling even next to white cotton.

The usefulness of shoddy cannot be doubted; it occupies a most important position in the manufacture of many lines of woolen textiles sold at prices that could not be otherwise produced for reasons previously indicated.

As to the pending legislative attempt to impose upon manufacturers the necessity of branding their goods, indicating the presence and amount of shoddy used, I do not propose to venture an opinion. In view of the fact that no known method exists whereby chemists or microscopists can definitely state whether a given fabric consists wholly or partly of shoddy, it is impossible to ascertain the amount contained in any fabric, although many attempts have been made from time to time to devise a practical method for determining its actual presence in fabrics, but without successful results.

It seems that the only way to accurately control the admixture of shoddy or regenerated wool fiber or other textile adulterant, so that the ultimate buyer of cloth could be assured as to what he is buying, would be to provide for the installation of some federal official in the mill, as is done in matters connected with the manufacture of fabrics for the Army, or in the animal products inspection service, and coupled with the final official branding of the finished article.

While the shoddy industry is small, it is essentially one that the chemical engineer can investigate with profit. It has been struggling along for many years without attracting a particle of scientific attention, and as a consequence has remained practically stationary except for a few very minor improvements to some of the machines employed. The carbonizing process alone offers a promising field for investigation and particularly in view of the constantly increasing prevalence of *silk* particles in rags, the presence of which offer distinct obstacles in cloth manufacturing, as many of the dyes used color the wool satisfactorily, but leave the silk only partially stained.

In conclusion, permit me to venture the assertion that the shoddy manufacturers are entitled to great respect and encouragement as belonging to the increasing army of conservationists so much needed in a new and fast growing country. The motto of the great Franklin: "A penny saved is a penny earned" might well be their shibboleth as making clear their right to the encouragement and coöperation of all economic factors.

## CHEMICAL ENGINEERING

By CHARLES S. PALMER

Received May 19, 1914

What is chemical engineering? The question is easily asked but no one seems to be quite sure of the right answer. As a branch of practice, distinct from civil, mechanical, or electrical engineering, chemical engineering is a recent affair, at least in public recognition, though the use of some of the principles and materials must be as old as civil engineering. It is not always necessary that a branch of manufacture or industry should be defined to be utilized; but in discussing the basic educational principles of a new department of engineering instruction and practice, it would be convenient to be able to have some provisional notion as a tentative guide.

When one is asked what chemical engineering is, he is apt to shrug his apologetic shoulders and to confess frankly that the chemical engineer is not a civil engineer, though he uses civil engineering, neither is the chemical engineer a mechanical or electrical engineer, though he uses the principles of both professions. Probably it is safe to state that the chemical engineer is one who uses any or all of the recognized branches of engineering, in order to work out a chemical idea. This chemical idea may be the main industrial plan under consideration, or it may be merely of secondary importance, and supplementary to some other idea. Thus, the chemical idea may be some such clearly outlined chemical scheme as the contact-process for the manufacture of sulfuric acid; or it may be an entirely subordinate problem such as softening the boiler water for a large steam-power plant. But, in either or both cases, there is some distinct chemical problem. This chemical problem means the clear conception of the end to be aimed at; the careful consideration of the theoretical side of this end; the detailed preparation of the engineering outfit required to carry out this plan; and the patient and systematic installation and operation of this outfit, with due regard to business economy, trade demands, and future possibilities. Now all this is so obvious that it sounds stupidly stale; but it is right here that the educational system is apt to fall down and fail to prepare the young chemical engineer for the real business.

It is one thing to plan a well devised scheme or what seems like a well devised scheme; it is quite another matter to carry this out to complete industrial operation. When the scheme is in the laboratory, the drafting room, and the consulting office, it may all seem to be about ninety-nine per cent worked out, and to need only about one per cent of application in order to complete it. But when the chemical and differential equation, the blueprint and the estimate get out onto the "job," the appearance is different. Then it begins to look as though the scheme is only about one per cent worked out, and that there remains about ninety-nine per cent for completion in real experience. In the planning, the chemical part looms up large; it looks as if the chemical part were nearly all of the plan. But when one comes to the erection and running of the required plant, the chemical part seems to shrink, and to be almost smothered by the mechanical phases of the plan. Yet this same chemical idea is at all times, for the chemical engineer, the central and governing idea of the whole scheme. It thus begins to appear that chemical engineering must have some unusually complex nature. There is a basic chemical idea; but, it must bow to, and in turn, control many other lines of materials, machines and men.

In planning a technical course for the study of chemical engineering, it becomes apparent that the chemical engineering teacher and student must have specially prepared and somewhat elaborate facilities and equipment. This equipment is so vast and varied that few teachers have the vision to see what is really needed, and still less the courage to insist on the proper meeting of the need.

Thus, it goes without the saying that the student should be trained to a reasonable degree in all the allied fundamentals of mathematics, physics, biology, drawing, language and business; he should be thoroughly trained in all the basic branches of chemistry, for that is his specialty; without being a specialist in any of these lines, for he is first and foremost and always to be a chemist, he should know enough of the outlines of civil, mechanical, and electrical engineering to use the civil, mechanical and electrical engineering materials needful to the work. And, on the engineering side of his study of his specialty, the chemical engineer must have a large assortment of commercial pieces of apparatus—from prime movers to power users, boilers, digesters, vacuum pans, multiple-effect evaporators, stills, extractors, centrifugal and plunger pumps, filters, dissolvers, agitators, precipitators, settlers, etc., etc.—in short, commercial examples of all the chief types of machines for the moving and control of solids, liquids, and gases, and particularly of "mud," the always present *bête noire* of the chemical engineer. Now these machines are made up of shafts, wheels, cogs, pulleys, belts, pipes, threads, valves, gaskets, etc., of many varieties. Furthermore, in real life, they all show a tendency to what old Dr Bushnell used to call "the total depravity of inanimate things." If there is any possible difficulty which can happen, that difficulty will happen with a regularity and persistency which is somewhat discouraging to the beginner. But the beginner must know how to take some of his machines apart, and how to repair and put them together. He must know, at least, how to direct the work of the repairing mechanic or helper who assists.

All this means that the chemical engineering laboratory is a shop of many and varied chemical machines, surrounded by carpenter, machine, pipe and tin shops, in which are the regular mechanics of these trades; here the student can learn to do many of the things, which will be of infinite necessity and help in his later practical work. This is true because the student must know not only how to use the machines which are of present and recognized use, but he must also know how to improve, adapt and combine any or all of these to new aims and uses.

This seems like a large demand for equipment; but, is it unreasonable? If it is true that chemical engineering is the newest, the most belated, and the most necessary just at present of all branches of engineering, the request is only reasonable. We have heard the name "chemical engineering" for some years; but, in all America, there are only two or three rationally ambitious attempts to plan and install such a laboratory. Yet the volume of trade manufacture directly dependent on chemical methods is now perhaps some seven billions of dollars, a sum roughly comparable with our agricultural production, which is rightly regarded as the basic industry of the country. This shows what is the need, and what is the neglect of training for the chemical industries in particular.

But, it may be said that if the actual value of chemical industries is already so great without any parallel development of chemical engineering education as a special training, what is the need for this new specialty? The answer is that these chemical industries have come from the natural use and abuse of our natural resources. That this use and this abuse are now being carried on with dreadful waste and delay; and that, in all engineering history, there was never such opportunity as awaits the rightly trained young chemical engineer. Not a careless word of criticism should be uttered against any one of the other well recognized branches of engineering. Indeed, this same seven-billion industry of chemical manufacture is at present only the sum total of civil, mechanical and electrical engineering, with some small shading of chemical service; but it all needs to have incorporated with it more of the chemical idea, not as a fad or a fifth wheel, but as an organic and fundamental part of the industry. It is absurd to suppose that chemistry can or



will overthrow any good part of engineering; but it should adapt, modify and develop as chance offers or need calls. Energy and power are going to waste on every side; raw materials and by-products are rotting or lying dormant all about us; thousands of inconveniences, dangers and necessities threaten, annoy and hinder us. Is there then no need for the chemist to join the full-back or the rush-line, and to get into real common-sense team-play?

But, granting that all this is literally true, who is to direct the organization and realization of the ideal and practical training school? There is but one great teacher in life and his name is "Experience." Says the Great Book, "Let not him that girdeth on the harness, boast himself as he that putteth it off;" and better still, "Let no one boast." The task is too great, too serious for pride or vanity to show its head. But Experience is a safe teacher. Why not then secure men who see from experience something of what is needed in this ambitious educational scheme and chance: men who have tried the practical side of things and who are willing, after successful history, to go back into the teaching laboratory, with something besides marks and percentages; such men are to be obtained; they should be used.

But, granting that the practical man of affairs is joined to the properly planned and generously installed laboratory for the right teaching of the right problems in the right way, even then the educational experiment is only begun. Civilization is a somewhat complex thing; and human nature is one of its most confusing elements. How are we to select the raw material for the right class of students to train for chemical engineers? And, how are we to train them right? There the big problems come in.

The chief question in industrial life is the frank and successful meeting of economic production. The unit of energy, the pound of matter, the dollar of capital, the day of labor—these make a practical compound which is worked out to industrial success in business. It is possible, in practical life, to appeal to the human side of the laborer so that he will produce economic results. How can we make the student, when and while he is a student of chemical engineering, see that in some way it is to his economic and social advantage to be sure that he is fitted to his choice? That he is not over-supplied with "yellow streaks" and a tendency to "cold feet," which will make the best opportunity for preparation only a huge joke and a melancholy farce? That is the problem; and it is a problem. But, like all other problems, it is amenable to study and solution.

We are not without examples of attempts to solve this problem. The part-time schools, as of Cincinnati and the General Electric at Lynn, are definite experiments along the right lines. Also, the suggestion that each school should itself run some line of manufacturing, is another; though perhaps that might seem to savor too much of a narrowing of training. But this principle certainly is safe, that a few things well learned are better than many things poorly or partly learned. And certainly, the more complete the mechanical acquaintance with obstinate machines, and the social acquaintance with obstinate men in the thoroughly equipped laboratory, so much the better will there result the inevitable weeding out of the unfit. Generalization followed by specialization may be part of the key; but perhaps the best clue to the solution may be found in Mr. Kipling's remark ("*The Maltese Cat*"), "Now a polo pony is like a poet; if he is born with a love for the game, he can be made."

23 PARK PLACE  
NEWTONVILLE, MASS.

## CHANDLER FOUNDATION LECTURE—1914

The Chandler Lectureship was inaugurated in Havemeyer Hall, Columbia University, on May 29th, during the celebration of the Fiftieth Anniversary of the founding of the School of Mines. Professor Emeritus Charles Frederick Chandler presided and introduced the lecturer, Dr. Leo H. Baekeland, whose address is printed in full below.

After a few words in appreciation of the importance of the lectureship and of the work of the speaker, President Nicholas Murray Butler presented to Dr. Baekeland the first impression of the Chandler Medal. [EDITOR.]

### SOME ASPECTS OF INDUSTRIAL CHEMISTRY

By L. H. BAEKELAND

While I appreciate deeply the distinction of speaking before you on the occasion of the Fiftieth Anniversary of the Columbia School of Mines, I realize, at the same time, that nobody here present could do better justice to the subject which has been chosen for this lecture than the beloved master in whose honor the Charles Frederick Chandler Lectureship has been created.

Dr. Chandler, in his long and eminently useful career as a professor and as a public servant, has assisted at the very beginning of some of the most interesting chapters of applied chemistry, here and abroad.

Some of his pupils have become leaders in chemical industry; others have found in his teachings the very conception of new chemical processes which made their names known throughout the whole world.

IS INDUSTRIAL CHEMISTRY A MERE MONEY-MAKING PROPOSITION?

Industrial chemistry has been defined as "the chemistry of dollars and cents." This rather cynical definition, in its narrower interpretation, seems to ignore entirely the far-reaching economic and civilizing influences which have been brought to life through

the applications of science; it fails to do justice to the fact that the whole fabric of modern civilization becomes, each day, more and ever more interwoven with the endless ramifications of applied chemistry. The earlier effects of this influence do not date back much beyond one hundred and odd years. They became distinctly evident during the first French Republic, increased under Napoleon, gradually spread to neighboring countries, and then reaching out farther, their influence is now obvious throughout the whole world.

#### CREATION OF FRENCH PATENT SYSTEM

France, during the revolution, scattered to the winds old traditions and conventionalities, in culture as well as in politics. Until then, she had mainly impressed the world by the barbaric, wasteful splendor of her opulent kings, at whose courts the devotees of science received scant attention in comparison with the more ornamental artists and belle-lettrists, who were petted and rewarded alongside of the all-important men of the sword. In fact, as far as the culture of science was concerned, the Netherlands, Germany and Italy, and more particularly, England, were head and shoulders above the France of "le Roi Soleil."

The struggles of the new régime put France in the awkward position of the legendary beaver which "had to climb a tree." If for no other reason, she needed scientists to help her in her wars against the rulers of other European nations. She needed them just as much for repairing her crippled finances and her badly disturbed industries which were dependent upon natural products imported until then, but of which the supply had suddenly been cut off by the so-called Continental Blockade. Money-prizes and other inducements had been offered for stimulating the development of chemical processes, and—what is more significant—patent laws were promulgated so as to foster invention.

Nicolas Leblanc's method for the manufacture of soda to replace the imported alkalis, Berthollet's method for bleaching with chlorine, the beet-sugar industry to replace cane sugar imported from the colonies, and several other processes, were proposed. All these chemical processes soon found themselves lifted from the hands of the secretive alchemist or the timid pharmacist to the rank of real manufacturing methods. Industrial chemistry had begun its lusty career.

First successes stimulated new endeavors and small wonder is it that France, with these favorable conditions at hand, for a while at least, entered into the most glorious period of that part of her history which relates to the development of chemistry, and the arts dependent thereon.

#### BACKWARD POSITION OF GERMANY

It is difficult to imagine that, at that time, Germany, which now occupies such an enviable position in chemistry, was so far behind, that even in 1822, when Liebig wanted to study chemistry at the best schools, he had to leave his own country and turn to Gay-Lussac, Thénard and Dulong in Paris.

#### DEVELOPMENT OF BRITISH CHEMICAL INDUSTRY

But the British were not slow to avail themselves of the new opportunities in chemical manufacturing so clearly indicated by the first successes of the French. Their linen bleacheries

and a modest balance were all that was needed to make nature give her answers.

#### DEVELOPMENT OF ORGANIC CHEMISTRY IN GERMANY

These modest paraphernalia, eloquent by their very simplicity, brought forth rapidly succeeding discoveries. One of them was truly sensational: Liebig and Wöhler succeeded in accomplishing the direct synthesis of urea; thinking men began to realize the far-reaching import of this revolutionary discovery whereby a purely organic substance had been created in the laboratory by starting exclusively with inorganic materials. This result upset all respected doctrines that organic substances are of a special enigmatic constitution, altogether different from inorganic or mineral compounds, and that they could be built up only by the agency of the so-called "vital force"—whatever that might mean.

Research in organic chemistry became more and more fascinating; all available organic substances were being investigated one after another by restless experimentalists.

Coal-tar, heretofore a troublesome by-product of gas manufacture, notwithstanding its uninviting, ill-smelling, black, sticky appearance, did not escape the general inquisitive tendency; some of its constituents, like benzol or others, were isolated and studied.

#### THE INFLUENCE OF KEKULÉ'S THEORY

Under the brilliant leadership of Kekulé, a successful attempt was made to correlate the rapidly increasing new experimental observations in organic chemistry into a new theory which would try to explain all the numerous facts, a theory which became the sign-post to the roads of further achievements.

**DISCOVERY OF ARTIFICIAL DYES**—The discovery of quickly succeeding processes for making from coal-tar derivatives numerous artificial dyes, rivaling, if not surpassing, the most brilliant colors of nature, made the group of bold investigators still bolder. Research in organic chemistry began to find rapid rewards; entirely new and successful industries based on purely scientific data were springing up in England and France, as well as in Germany. Some wide-awake leaders of these new enterprises, more particularly in Germany, soon learned that they were never hampered by too much knowledge, but that, on the contrary, they were almost continuously handicapped in their impatient onward march by insufficient knowledge, or by misleading conceptions, if not by incorrect published facts. This is precisely where the study of organic chemistry received its greatest stimulating influence and soon put Germany, in this branch of science, ahead of all other nations.

Money and effort had to be spent freely for further research. The best scholars in chemistry were called into action. Some men, who were preparing themselves to become professors, were induced to take a leading part as directors in one or another of the new chemical enterprises. Others, who refused to forsake their teaching careers, were retained as advisers or guides, and, in several instances, the honor of being the discoverer of a new process, or a new dye, was made more substantial by financial rewards. The modest German university professor, who heretofore had lived within a rather narrow academic sphere, went through a process of evolution, where the rapidly growing chemical industry made him realize his latent powers and greater importance, and broadened his influence far beyond the confines of his lecture-room. Even if he were altruistic enough to remain indifferent to fame or money, he felt stimulated by the very thought that he was helping, in a direct manner, to build up the nation and the world through the immediate application of the principles of science.

#### INDUSTRIAL RESEARCH LABORATORIES

In the beginning, science did all the giving and chemical industry got most of the rewards; but soon the rôles began to change to the point where frequently they became entirely inverted.



THE CHARLES FREDERICK CHANDLER MEDAL

in Scotland and England soon used an improved method for bleaching with chloride of lime, developed by Tennant, which brought along the manufacture of other chemicals relating thereto like sulfuric acid and soda. The chemical reactions involved in all these processes are relatively simple, and after they were once well understood, it required mainly resourceful engineering and good commercial abilities to build up successfully the industries based thereon. From this epoch on dates the beginning of the development of that important industry of heavy chemicals in which the British led the world for almost a century. In the same way, England had become the leader in another important branch of chemical industry—the manufacture of coal-gas.

#### LIEBIG'S INFLUENCE IN GERMANY

The Germans were soon to make up for lost time. Those same German universities, which when Liebig was a young man were so poorly equipped for the study of chemistry, were now enthusiastically at work on research along the newer developments of the physical sciences, and, before long, the former pupils of France, in their turn, became teachers of the world. Liebig had inaugurated for the chemical students working under him his system of research laboratories; however modest these laboratories may have been at that time, they carried bodily the study of chemistry from pedagogic boresomeness into a captivating cross-examination of nature.

And it seemed as if nature had been waiting impatiently to impart some of her secrets to the children of men, who for so many generations had tried to settle Truth and Knowledge by words and oratory and by brilliant displays of metaphysical controversies. Indeed, at that time, a few kitchen tables, some clumsy glassware, a charcoal furnace or two, some pots and

The universities did not furnish knowledge fast enough to keep pace with the requirements of the rapidly developing new industries. Modern research laboratories were organized by some large chemical factories on a scale never conceived before, with a lavishness which made the best equipped university laboratory appear like a timid attempt. Germany, so long behind France and England, had become the recognized leader in organic manufacturing processes and developed a new industrial chemistry based more on the thorough knowledge of organic chemistry than on engineering skill.

In this relation, it is worth while to point out that the early organic industrial chemistry, through which Germany was soon to become so important, at first counted its output not in tons, but in pounds—not in size nor in quantity, but in variety and quality. Now let us see how Germany won her spurs in chemical engineering as well.

#### DEVELOPMENT OF CHEMICAL ENGINEERING IN GERMANY

At the beginning, the manufacturing problems in organic chemistry involved few, if any, serious engineering difficulties, but required, most of all, a sound theoretical knowledge of the subject; this put a premium on the scientist, and the engineer could be ignored for awhile at least. But when growing developments began to claim the help of good engineers, there was no difficulty whatsoever in supplying them, nor in making them cooperate with the scientists. In fact, since then, Germany has solved, just as successfully, some of the most extraordinary chemical engineering problems ever undertaken, although the development of such processes was entered upon at first from the purely scientific side.

In almost every case, it was only after the underlying scientific facts had been well established that any attempt was made to develop them commercially.

#### METHODS OF HEALTHY DEVELOPMENT OF SCIENTIFIC PROCESSES

Healthy commercial development of new scientific processes does not build its hope of success upon the cooperation of that class of "promoters" which are always eager to find any available pretext for making "quick money," and whose scientific ignorance contributes conveniently to their comfort by not interfering too much with their self-assurance and their voluble assertions. The history of most of the successful recent chemical processes abounds in examples where, even after the underlying principles were well established, long and costly preparatory team-work had to be undertaken; where foremost scientists, as well as engineers of great ability, had to combine their knowledge, their skill, their perseverance, with the support of large chemical companies, who, in their turn, could rely on the financial backing of strong banking concerns, well advised by tried expert specialists.

History does not record how many processes thus submitted to careful study were rejected because, on close examination, they were found to possess some hopeless shortcomings. In this way, numerous fruitless efforts and financial losses were averted, where less carefully accumulated knowledge might have induced less scrupulous promoters to secure money for plausible but ill-advised enterprises.

**SYNTHESIS OF INDIGO.**—In the history of the manufacture of artificial dyes, no chapter gives a more striking instance of long, assiduous and expensive preliminary work of the highest order than the development of the industrial synthesis of indigo. Here was a substance of enormous consumption which, until then, had been obtained from the tropics as a natural product of agriculture. Professor von Baeyer and his pupils, by long and marvelously clever laboratory work, succeeded finally in unraveling the chemical constitution of this indigo dye, and finally indicated some possible methods of synthesis. Notwithstanding all this, it took the Badische Anilin & Soda Fabrik about twenty years of patient research work, carried

out by a group of eminent chemists and engineers, before a satisfactory method was devised by which the artificial product could compete in price and in quality with natural indigo.

**INFLUENCES OF A GOOD PATENT SYSTEM.**—Germany with her well administered and easily enforceable patent laws, has added, through this very agency, a most vital inducement for pioneer work in chemical industries. Who otherwise would dare to take the risk of all the expenses connected with this class of creative work? Moreover, who would be induced to publish the result of his discoveries far and wide throughout the whole world in that steadily flowing stream of patent literature, which, much sooner than any text-books or periodicals, enables one worker to be benefited and to be inspired by the publication of the latest work of others?

#### INTERNATIONAL SCOPE OF CHEMICAL RESEARCH

The development of some problems of industrial chemistry has enlisted the brilliant collaboration of men of so many different nationalities that the final success could not, with any measure of justice, be ascribed exclusively to one single race or nation; this is best illustrated by the invention of the different methods for the fixation of nitrogen from the air.

This extraordinary achievement, although scarcely a few years old, seems already an ordinary link in the chain of common, current events of our busy life; and yet, the facts connected with this recent conquest reveal a modern tale of great deeds of the race—an Epos of Applied Science. Its story began the day when chemistry taught us how indispensable are the nitrogenous substances for the growth of all living beings.

#### DEFICIENCY OF NITROGEN FERTILIZERS IN AGRICULTURE

Generally speaking, the most expensive foodstuffs are precisely those which contain most nitrogen, for the simple reason that there is, and always has been, at sometime or another, a shortage of nitrogenous foods in the world. Agriculture furnishes us these proteid- or nitrogen-containing bodies, whether we eat them directly as vegetable products, or indirectly as animals which have assimilated the proteids from plants. It so happens, however, that by our ill-balanced methods of agriculture, we take nitrogen from the soil much faster than it is supplied to the soil through natural agencies. We have tried to remedy this discrepancy by enriching the soil with manure or other fertilizers, but this has been found totally insufficient, especially with our methods of intensive culture—our fields want more nitrogen. So agriculture has been looking anxiously around to find new sources of nitrogen fertilizer. For a short time, an excellent supply was found in the guano deposits of Peru; but this material was used up so eagerly that the supply lasted only a very few years. In the meantime, the ammonium salts recovered from the by-products of the gas-works have come into steady use as nitrogen fertilizer. But, here again, the supply is entirely insufficient, and during the later period our main reliance has been placed on the natural beds of sodium nitrate which are found in the desert regions of Chile. This has been, of late, our principal source of nitrogen for agriculture, as well as for the many industries which require saltpeter or nitric acid.

#### CHILE SALTPETER AND ITS APPROACHING EXHAUSTION

In 1898, Sir William Crookes, in his memorable presidential address before the British Association for the Advancement of Science, called our attention to the threatening fact that, at the increasing rate of consumption, the nitrate beds of Chile would be exhausted before the middle of this century. Here was a warning—an alarm call—raised to the human race by one of the deepest scientific thinkers of our generation. It meant no more nor less than that before long our race would be confronted with nitrogen starvation. In a given country, all other conditions being equal, the abundance or the lack of nitrogen available for nutrition is a paramount factor in the degree of general welfare, or of physical decadence. The less



nitrogen there is available as foodstuffs, the nearer the population is to starvation. The great famines in such nitrogen-deficient countries as India and China and Russia are sad examples of nitrogen starvation.

And yet, nitrogen, as such, is so abundant in nature that it constitutes four-fifths of the air we breathe. Every square mile of our atmosphere contains nitrogen enough to satisfy our total present consumption for over half a century. However, this nitrogen is unavailable as long as we do not find means to make it enter into some suitable chemical combination. Moreover, nitrogen was generally considered inactive and inert, because it does not enter readily in chemical combination.

William Crookes' disquieting message of rapidly approaching nitrogen starvation did not cause much worry to politicians—they seldom look so far ahead into the future. But, to the men of science, it rang like a reproach to the human race. Here, then, we were in possession of an inexhaustible store of nitrogen in the air, and yet, unless we found some practical means for tying some of it into a suitable chemical combination, we would soon be in a position similar to that of a shipwrecked sailor, drifting around on an immense ocean of brine, and yet slowly dying for lack of drinking water.

#### OXIDATION OF AIR NITROGEN

**THE PRIESTLEY-CAVENDISH EXPERIMENT**—As a guiding beacon, there was, however, that simple experiment, carried out in a little glass tube, as far back as 1785, by both Cavendish and Priestley, which showed that if electric sparks were passed through air, the oxygen thereof was able to burn some of the nitrogen and to engender nitrous vapors.

**BRADLEY AND LOVEJOY**—This seemingly unimportant laboratory curiosity, so long dormant in the text-books, was made a starting point by Charles S. Bradley and D. R. Lovejoy, in Niagara Falls, for creating the first industrial apparatus for converting the nitrogen of the air into nitric acid by means of the electric arc. As early as 1902, they published their results as well as the details of their apparatus. Although they operated only one full-sized unit, they demonstrated conclusively that nitric acid could thus be produced from the air in unlimited quantities. We shall examine later the reasons why this pioneer enterprise proved a commercial success; but to these two American inventors belongs, undoubtedly, the credit of having furnished the first answer to the distress call of Sir William Crookes.

**BIRKELAND AND EYDE**—In the meantime, many other investigators were at work at the same problem, and soon from Norway's abundant waterfalls came the news that Birkeland and Eyde had solved successfully, and on a commercial scale, the same problem by a differently constructed apparatus.

**PAULING AND SCHOENHERR**—The Germans, too, were working on the same subject, and we heard that Schoenherr, also Pauling, had evolved still other methods, all, however, based on the Cavendish-Priestley principle of oxidation of nitrogen. In Norway alone, the artificial saltwater factories use now, day and night, over 200,000 electrical horse-power, which will soon be doubled; while a further addition is contemplated which will bring the volume of electric current consumed to about 500,000 horse-power. The capital invested at present in these works amounts to \$27,000,000.

#### CYANAMIDE

Frank and Caro, in Germany, succeeded in creating another profitable industrial process whereby nitrogen could be fixed by carbide of calcium, which converts it into calcium cyanamide, an excellent fertilizer by itself. By the action of steam on cyanamide, ammonia is produced, or it can be made the starting point of the manufacture of cyanides, so profusely used for the treatment of gold and silver ores.

Although the synthetic nitrates have found a field of their own, their utilization for fertilizers is smaller than that of the cyanamide; and the latter industry represents, today, an invest-

ment of about \$30,000,000, with three factories in Germany, two in Norway, two in Sweden, one in France, one in Switzerland, two in Italy, one in Austria, one in Japan, one in Canada, but not any in the United States. The total output of cyanamide is valued at \$15,000,000 yearly and employs 200,000 horse-power, and preparations are made at almost every existing plant for further extensions. An English company is contemplating the application of 1,000,000 horse-power to the production of cyanamide and its derivatives, 600,000 of which have been secured in Norway and 400,000 in Iceland.

#### NITRIDE PROCESSES

But still other processes are being developed, based on the fact that certain metals or metalloids can absorb nitrogen, and can thus be converted into nitrides; the latter can either be used directly as fertilizers or they can be made to produce ammonia under suitable treatment.

**SERPKE PROCESS**—The most important of these nitride processes seems to be that of Serpke, who, in his experimental factory at Niedermorschweiler, succeeded in obtaining aluminum nitride in almost theoretical quantities, with the use of an amount of electrical energy eight times less than that needed for the Birkeland-Eyde process and one-half less than for the cyanamide process, the results being calculated for equal weights of "fixed" nitrogen. A French company has taken up the commercial application of this process which can furnish, besides ammonia, pure alumina for the manufacture of aluminum metal.

#### HABER'S PROCESS FOR AMMONIA

An exceptionally ingenious process for the direct synthesis of ammonia, by the direct union of hydrogen with nitrogen, has been developed by Haber in conjunction with the chemists and engineers of the Badische Anilin & Soda Fabrik. The method has the advantage that it is not, like the other nitrogen-fixation processes, paramountly dependent upon cheap power; for this reason, if for no other, it seems to be destined to a more ready application. The fact that the group of the three German chemical companies which control the process have sold out their former holdings in the Norwegian enterprises to a Norwegian-French group, and are now devoting their energies to the commercial installation of the Haber process, has quite some significance as to expectations for the future.

#### THE FUTURE OF NITROGEN-FIXATION PROCESSES

The question naturally arises: Will there be an overproduction and will these different rival processes not kill each other in slaughtering prices beyond remunerative production? Nitrogen fertilizers are already used at the rate of about \$200,000,000 worth a year, and any decrease in price, and, more particularly, better education in farming, will probably lead to an enormously increased consumption. It is worth mentioning here that, in 1825, the first ship-load of Chile saltwater which was sent to Europe could find no buyer, and was finally thrown into the sea as useless material. Then again, processes for nitric acid and processes for ammonia, instead of interfering, are supplementary to each other, because the world needs ammonia and ammonium salts, as well as nitric acid or nitrates. It should be pointed out also, that, ultimately, the production of ammonium nitrate may prove the most desirable method to minimize freight, for this salt contains much more nitrogen to the ton than does the more bulky calcium salt in which form synthetic nitrates are now marketed.

#### WHY DID BRADLEY AND LOVEJOY NOT SUCCEED?

Before leaving this subject, let us examine why Bradley and Lovejoy's efforts came to a standstill where others succeeded.

First of all, the cost of power at Niagara Falls is three to five times higher than in Norway, and although at the time this was not strictly prohibitive for the manufacture of nitric acid, it was entirely beyond hope for the production of fertilizers. The relatively high cost of power in our country is the reason why

the cyanamide enterprise had to locate on the Canadian side of Niagara Falls, and why, up till now, outside of an experimental plant in the South (a 4000 horse-power installation in North Carolina, using the Pauling process), the whole United States has not a single synthetic nitrogen fertilizer works.

The yields of the Bradley-Lovejoy apparatus were rather good. They succeeded in converting as much as  $2\frac{1}{2}$  per cent of the air, which is somewhat better than their successors are able to accomplish. But their units, 12 kilowatts, were very much smaller than the 1000 to 3000 kilowatts now used in Norway and they were also more delicate, all of which made installation and operation considerably more expensive. However, this was the natural phase through which any pioneer industrial development has to go, and it is more than probable that in the natural order of events these imperfections would have been eliminated. But the killing stroke came when financial support was suddenly withdrawn.

#### NECESSITY OF SCIENTIFIC TEAM-WORK AND GOOD FINANCIAL BACKING

In the successful solution of similar industrial problems, the originators in Europe were not only backed by scientifically well-advised bankers, but they were helped to the rapid solution of all the side problems by a group of specially selected scientific collaborators, as well as by all the resourcefulness of well-established chemical enterprises.

That such conditions are possible in the United States has been demonstrated by the splendid team-work which led to the development of the modern tungsten lamp in the research laboratories of the General Electric Company, and to the development of the Tesla polyphase motor by the group of engineers of the Westinghouse Company.

True, there are endless subjects of research and development which can be brought to success by the efforts of single independent inventors, but there are some problems of applied science which are so vast, so much surrounded with ramifying difficulties, that no one man, nor two men, however exceptional, can either furnish the brains or the money necessary for leading to success within a reasonable time. For such special problems, the rapid coöperation of numerous experts and the financial resources of large establishments are indispensable.

#### DOLLARS AND CENTS A CRITERION OF EFFICIENCY

All these examples of the struggle for efficiency and improvement demonstrate why, in industrial chemistry, the question of *dollars and cents* has to be taken very much into consideration. From this standpoint at least, the "Dollars and cents" argument can be interpreted as a symptom of industrial efficiency, and thus, the definition sounds no longer as a reproach. With some allowable degree of accuracy, it formulates one of the economic aspects of any acceptable industrial chemical process. Indeed, barring special conditions, as, for instance, incompetent or reckless management, unfair competition, monopolies, or other artificial privileges, the money success of a chemical process is the cash plebiscite of approval of the consumers. It is bound, after a time at least, to weed out the inefficient methods.

#### INFLUENCE OF SECONDARY FACTORS IN CHEMICAL PROCESSES

Some chemists, who have little or no experience with industrial enterprises, are too much over-inclined to judge a chemical process exclusively from the standpoint of the chemical reactions involved therein, without sufficient regard to engineering difficulties, financial requirements, labor problems, market and trade conditions, rapid development of the art involving frequent disturbing improvements in methods and expensive changes in equipment, advantages or disadvantages of the location of the plant, and other conditions so numerous and variable that many of them can hardly be foreseen even by men of experience. And yet, these seemingly secondary considerations most of the time become the deciding factor of success or failure of an otherwise well-conceived chemical process.

**FREIGHT**—The cost of transportation alone will frequently decide whether a certain chemical process is economically possible or not. For instance, the big Washoe Smelter, in Montana, wastes enough sulfur dioxide gas to make daily 1800 tons of sulfuric acid, but that smelter is too far distant from any possible market for such a quantity of otherwise valuable material. Another example is found in the natural deposits of soda, or soda lakes, in California. One of these soda lakes contains from thirty to forty-two million tons of soda. Here is a natural source of supply which would be ample to satisfy the world's demand for many years to come. Similar deposits exist in other parts of the world, but the cost of transportation to a sufficiently large and profitable market is so exorbitant that, in the meantime, it is cheaper to erect, at more convenient points, expensive chemical works in which soda is made chemically and from which the market can be supplied more profitably. In addition, we can cite the artificial nitrate processes in Norway, which, notwithstanding their low efficiency and expensive installation, can furnish nitrate in competition with the natural nitrate beds of Chile, because the latter are hampered by the cost of extraction from the soil where fuel for crystallization is expensive, in addition to the considerable cost of freight.

**THE LEBLANC SODA PROCESS**—But there is no better example, illustrating the far-reaching effect of seemingly secondary conditions upon the success of a chemical process, than the history of the Leblanc soda process. This famous process was the fore-runner of chemical industry: for almost a century it dominated the enormous group of industries of heavy chemicals so expressively called by the French: "*La Grande Industrie Chimique*," and now we are witnesses of the lingering death agonies of this chemical colossus. Through the Leblanc process, large fortunes have been made and lost; but even after its death, it will leave a treasure of information to science and chemical engineering, the value of which can hardly be overestimated.

Here, then, is a very well worked-out process, admirably studied in all its details, which, in its heroic struggle for existence, has drawn upon every conceivable resource of ingenuity furnished by the most learned chemists and the most skillful engineers, who succeeded in bringing it to an extraordinary degree of perfection, and which, nevertheless, has to succumb before inexorable although seemingly secondary, conditions.

**SOLVAY SODA PROCESS**—Strange to say, its competitor, the Solvay process, entered into the arena after a succession of failures. When Solvay, as a young man, took up this process, he was totally ignorant of the fact that no less than about a dozen able chemists had invented and reinvented the very reaction on which he had pinned his faith; that, furthermore, some had tried it on a commercial scale, and had, in every instance, encountered failure. At that time, all this must, undoubtedly, have been to young Solvay a revelation sufficient to dishearten almost anybody. But he had one predominant thought to which he clung as a last hope of success, and which would probably have escaped most chemists; he reasoned that he started from two watery solutions, which, when brought together, precipitate a dry product, bicarbonate of soda, while in the Leblanc process, the raw materials must be melted together, with the use of expensive fuel, after which the mass is dissolved in water, losing all these valuable heat units, while more heat has again to be applied for evaporation to dryness.

After all, most of the weakness of the Leblanc process resides in the greater consumption of fuel. But the cost of fuel, here again, is determined by freight rates. This is so true that we find that the last few Leblanc works which manage to keep alive are exactly those which are situated near unusually favorable shipping points, where they can obtain cheap fuel, as well as cheap raw materials, and whence they can most advantageously reach certain profitable markets. But another tremendous handicap of the Leblanc process is that it



gives as one of its by-products, hydrochloric acid. Profitable use for this acid, as such, can be found only to a limited extent. It is true that hydrochloric acid could be used in much larger quantities for many purposes where sulfuric acid is used now, but it has, against sulfuric acid, a great freight disadvantage. In its commercially available condition, it is an aqueous solution, containing only about one-third of real acid, so that the transportation of one ton of acid practically involves the extra cost of freight of about two tons of water. Furthermore, the transportation of hydrochloric acid in anything but glass carboys involves very difficult problems in itself, so that the market for hydrochloric acid remains always within a relatively small zone from its point of production. However, for a while at least, an outlet for this hydrochloric acid was found by converting it into a dry material which can easily be transported; namely, chloride of lime or bleaching powder.

**ELECTROLYTIC PROCESSES A NEW COMPETITOR**—The amount of bleaching powder consumed in the world practically dictated the limited extent to which the Leblanc process could be profitably worked in competition with the Solvay process. But even this outlet has been blocked during these later years by the advent of the electrolytic alkali processes, which have sprung up successfully in several countries, and which give, as a cheap by-product, chlorine, which is directly converted into chloride of lime. Today, any process which involves the production of large quantities of hydrochloric acid, beyond what the market can absorb as such, or as derivatives thereof, becomes a positive detriment, and foretells failure of the process. Even if we could afford to lose all the acid, the disposal of large quantities of it conflicts immediately with laws and ordinances relative to the pollution of the atmosphere or streams, or the rights of neighbors, and occasions expensive damage suits.

**MARKET FOR CHLORINE PRODUCTS**—Whatever is said about hydrochloric acid, applies, to some extent, to chlorine, produced in the electrolytic manufacture of caustic soda. Here again, the development of the latter industry is limited, primarily, by the amount of chlorine which the market can absorb, as such, or as chlorinated products. At any rate, chlorine can be produced much cheaper by electrolytic caustic alkali processes than formerly, and in the meantime the market price of chloride of lime has already been cut about in half.

#### ALKALI INDUSTRY IN THE UNITED STATES

Since the rather young electrolytic alkali industry has taken a considerable development in the United States, let us examine it somewhat more closely. At present, the world's production of chloride of lime approximates about half a million tons. We used to import all our chloride of lime from Europe, until about fifteen years ago, when the first successful electrolytic alkali works were started at Niagara Falls. That ingenious mercury cell of Hamilton V. Castner—a pupil of Professor Chandler and one of the illustrious sons of the Columbia School of Mines—was first used, and his process still furnishes a large part of all the electrolytic caustic soda and chlorine manufactured here and abroad.

At present, about 30,000 electrical horse-power are employed uninterruptedly for the different processes used in the United States, and our home production has increased to the point where, instead of importing chloride of lime, we shall soon be compelled to export our surplus production. It looks now as if, for the moment at least, any sudden considerable increase in the production of chloride of lime would lead to overproduction unless new channels of consumption of chloride of lime or other chlorine products can be found.

**NEW USES FOR CHLORINE**—However, new uses for chlorine are being found every day. The very fact that commercial hydrochloric acid of exceptional purity is now being manufactured in Niagara Falls by starting from chlorine, indicates clearly that conditions are being reversed; no longer than a few years ago,

when chlorine was manufactured exclusively by means of hydrochloric acid, this would have sounded like a paradox.

The consumption of chlorine for the preparation of organic chlorination products utilized in the dye-stuff industry, is also increasing continually, and its use for the manufacture of tetrachloride of carbon and so-called acetylene chlorination products, has reached quite some importance.

There is probably a much overlooked but wider opening for chlorinated solvents in the fact that ethylene gas can be prepared now at considerably lower cost than acetylene, and that ethylene chloride, the well-known "Dutch Liquid," is an unusually good solvent. It has, furthermore, the great advantage that its specific gravity is not too high, and its boiling point, too, is about the right temperature. It ought to be possible to make it at such a low price that it would find endless applications where the use of other chlorination solvents has thus far been impossible.

The chlorination of ores for certain metallurgical processes may eventually open a still larger field of consumption for chlorine.

In the meantime, liquefied chlorine gas, obtained by great compression, or by intense refrigeration, has become an important article of commerce, which can be transported in strong steel cylinders. Its main utilization resides in the manufacture of tin chloride by the Goldschmidt process for reclaiming tin-scrap. It is finding, also, increased applications as a bleaching agent and for the purification of drinking water, as well as for the manufacture of various chlorination products.

Its great handicap for rapid introduction is again the question of freight, since heavy and expensive containers are indispensable.

**FREIGHT PROBLEM IN RELATION TO CHLORINE**—In most cases, the transportation problem of chlorine is solved more economically by handling it as chloride of lime, which, after all, represents chlorine or oxygen in solid form, easily transportable. It would seem as if the freight difficulty could easily be eliminated by producing the chlorine right at the spot of consumption. But this is not always so simple as it may appear. To begin with, the cost of an efficient plant for any electrolytic operation is always unusually high as compared with other chemical equipments. Then, also, small electrolytic alkali plants are not profitable to operate. Furthermore, the conditions for producing cheap chlorine depend on many different factors, which all have to coordinate advantageously; for instance, cheap power, cheap fuel, and cheap raw materials are essential, while, at the same time, a profitable outlet must be found for the caustic soda.

Lately, there has been a considerable reduction of the market price of caustic soda which may cause the gradual elimination of the less efficient electrolytic processes; however, this may not necessarily be the case for smaller plants which do not compete in the open market, but consume their own output for some special purpose.

#### ELECTROLYTIC ALKALI CELLS

Several distinct types of electrolytic alkali cells are now in successful use, but experience seems to demonstrate that the so-called diaphragm cells are cheapest to construct and to operate, provided, however, that no exception be taken to the fact that this caustic soda always contains some sodium chloride, usually varying from 2 to 3 per cent, which it is not practical to eliminate; for almost all commercial purposes the presence of this impurity is of no importance.

Mercury cells give a much purer caustic soda, and this may, in some cases, compensate for their more expensive equipment and operation. Moreover, there are some operations where the initial caustic solution of rather high concentration, produced directly in these cells, can be used as it is, thus obviating further concentration and cost of fuel.

The expenses for evaporation and elimination of salt from the raw caustic solutions increase to an exaggerated extent with some



types of diaphragm cells, which produce only very weak caustic liquors. This is also the case with the so-called "gravity cell," sometimes called the "bell type," or "Aussig type," of cell. But these gravity cells have the merit of dispensing with the delicate and expensive problem of diaphragms. On the other hand, their units are very small, so that they necessitate a rather complicated installation occupying an unusually large floor space and expensive buildings.

The general tendency is now toward cells which can be used in very large units, which can be housed economically, and of which the general cost of maintenance and renewal is small; some of the modern types of diaphragm cells are now successfully operating with 3000 to 5000 amperes per cell.

As to the possible future improvements in electrolytic alkali cells, we should mention that in some types the current efficiencies have practically reached their maximum, and average ampere efficiencies as high as 95 to 97 per cent have been obtained in continuous practice. The main difficulty is to reinforce these favorable results by the use of lower voltage, without making the units unnecessarily bulky or expensive in construction or in maintenance—all factors which soon outweigh any intended saving of electric current. Here, more than in any other branch of chemical engineering, it is easy enough to determine how "good" a cell is on a limited trial, but it takes expensive, long-continued use on a full commercial scale, running uninterruptedly day and night for years, to find out how "bad" it is for real commercial practice.

#### CHEAP POWER NOT THE ONLY FACTOR

In relation to the electrolytic alkali industry, a great mistake is frequently made by considering the question of power as paramount; true enough, cheap power is very important, almost essential, but certainly it is not everything. There have been cases where it was found much cheaper in the end to pay almost double for electric current in a certain locality, than in another site not far distant from the first, for the simple reason that the cheaper power supply was hampered by frequent interruptions and expensive disturbances, which more than offset any possible saving in cost of power. In further corroboration, it is well known that some of the most successful electrolytic soda manufacturers have found it to their advantage to sacrifice power by running their cells at decidedly higher voltage than is strictly necessary—which simply means consuming more power; this is done to be able to use higher current densities, thereby increasing considerably the output of the same size units, economizing on the general cost of plant operation. Here is one of the ever-recurring instances in chemical manufacturing where it becomes more advantageous to sacrifice apparent theoretical efficiency in favor of industrial expediency. All this does not diminish the fact that the larger electrochemical industries can thrive only where cheap power is available.

#### IMPORTANCE OF CHEAP POWER FOR ELECTROCHEMICAL PROCESSES

Modern progress of electrical engineering has given us the means to utilize so-called natural powers; until now, however, we have availed ourselves only of the water-power developed from rivers, lakes, and waterfalls. As far as larger electric power generation is concerned, the use of the wind, or the tide, or the heat of the sun, represents, up till now, nothing much beyond a mere hope of future possibilities.

In the meantime, it so happens, unfortunately, that many of the most abundant water-powers of the world are situated in places of difficult access, far removed from the zone of possible utilization.

#### COST OF WATER-POWER IN THE UNITED STATES STILL TOO HIGH

But, precisely on this account, it would appear, at first sight, as if the United States, with some of her big water-powers situated nearer to active centers of consumption, would be in an exceptionally favorable condition for the development of electro-

chemical industries. On closer examination, we find, however, that the cost of water-power, as sold to manufacturers, is, in general, much higher than might be expected; at any rate, it is considerably more expensive than the cost of electric power utilized in the Norway nitrate enterprises. This is principally due to the fact that in the United States, water-power, before it is utilized by the electrolytic manufacturer, has really to pay one, two, and sometimes three, profits, to as many intermediate interests, which act as so many middlemen between the original water-power and the consumer. Only in such instances as in Norway, where the electrochemical enterprise and the development of the water-power are practically in the same hands, can electric current be calculated as its real cheapest cost.

Neither should the fact be overlooked that the best of our water-powers in the East are situated rather far inland. Although this does not matter much for the home market, it puts us at a decided disadvantage for the exportation of manufactured goods, in comparison again with Norway, where the electrolytic plants are situated quite close to a good sea-harbor open in all seasons.

#### INCREASING USE OF WASTE GAS AND PRODUCER GAS

Some electrochemical enterprises require cheap fuel just as much as cheap power; and, on this account, it has proved sometimes more advantageous to dispense entirely with water-power by generating gas for fuel as well as for power from cheap coal or still cheaper peat.

At present, most of our ways of using coal are still cumbersome and wasteful, although several efficient methods have been developed which some day will probably be used almost exclusively, principally in those places where lower grades of cheap coal are obtainable.

MOND-GAS—I refer here particularly to the valuable pioneer work of that great industrial chemist, Mond, on cheap water-gas production, by the use of a limited amount of air in conjunction with water vapor.

More recently, this process has been extended by Caro, Frank and others, to the direct conversion of undried peat into fuel-gas.

By the use of these processes, peat or lower grades of coal, totally unsuitable for other purposes, containing, in some instances, as much as 60 to 70 per cent of incombustible constituents, can be used to good advantage in the production of fuel for power generation.

Whether Mond-gas will ever be found advantageous for distribution to long distances is questionable, because its heating value per cubic foot is rather less than that of ordinary water-gas, but this does not interfere with its efficient use in internal combustion engines.

In general, our methods for producing or utilizing gas in our cities do scant justice to the extended opportunities indicated by our newer knowledge.

#### ANTIQUED MUNICIPAL SPECIFICATIONS FOR GAS TESTING

Good fuel-gas could be manufactured and distributed to the individual household consumer at considerably cheaper rates, if it were not for antiquated municipal specifications, which keep on prescribing photometric tests instead of insisting on standards of fuel value, which makes the cost of production unnecessarily high, and disregards the fact that, for lighting, the Welsbach mantle has rendered obsolete the use of highly carbureted gas as a bare flame. But for those unfortunate specifications, cheap fuel-gas might be produced at some advantageous central point, where very cheap coal is available; such heating gas could be distributed to every house and every factory, where it could be used cleanly and advantageously, like natural gas, doing away at once with the black coal smoke nuisance, which now practically compels a city like New York to use nothing but the more expensive grades of anthracite coal. It would eliminate, at the same time, all the bother and expense caused through the clumsy

and expensive methods of transportation and handling of coal and ashes; it would relieve us from many unnecessary middlemen who now exist between coal and its final consumer.

#### NEW POWER CENTERS TO COMPETE WITH WATER-POWER

The newer large-sized internal combustion engines are introducing increasing opportunities for new centers of power production where waste gas of blast-furnaces or coke-ovens, or where deposits of inferior coal or peat, are available.

If such centers are situated near tidewater, this may render them still more advantageous for some electrochemical industries, which, until now, were compelled to locate near some inland water-powers.

**INCREASED PRODUCTION OF AMMONIA AND OTHER BY-PRODUCTS FROM GAS**—Nor should we overlook the fact that the newer methods for the production of cheap fuel-gas offer excellent opportunities for an increased production of valuable tar by-products, and more particularly of ammonium salts; the latter would help to a not inconsiderable extent in furnishing more nitrogen fertilizer.

It is somewhat remarkable that a greater effort has already been made to start the industrial synthesis of nitrogen products than to economize all these hitherto wasted sources of ammonia.

#### OUR UNBALANCED METHODS OF AGRICULTURE

In fact, science indicates still other ways, somewhat of a more radical nature, for correcting the nitrogen deficiencies in relation to our food supply.

Indeed, if we look well at this matter from a much broader standpoint, we may find that, after all, the shortage of nitrogen in the world is attributable, to a large extent, to our rather one-sided system of agriculture. We do not sufficiently take advantage of the fact that certain plants, for instance those of the group of Leguminosae, have the valuable property of easily assimilating nitrogen from the air, without the necessity of nitrogen fertilizers. In this way, the culture of certain Leguminosae can insure enough nitrogen for the soil, so that, in rotation with nitrogen-consuming crops, like wheat, we could dispense with the necessity of supplying any artificial nitrogen fertilizer.

#### DISTURBING INFLUENCE OF RAISING TOO MANY CATTLE

The present nitrogen deficiency is influenced further by two other causes. The first cause is our unnecessarily exaggerated meat diet in which we try to find our proteid requirements, and which compels us to raise so many cattle, while the amount of land which feeds one head of cattle could furnish, if properly cultivated, abundant vegetable food for a family of five. The second cause is our insufficient knowledge of the way to grow and prepare for human food just those vegetables which are richest in proteids. Unfortunately, it so happens that exactly such plants as, for instance, the soy-bean, are not by any means easily rendered palatable and digestible, while any savage can eat raw meat, or can readily cook, boil or roast it for consumption.

On this subject, we can learn much from some Eastern people, like the Japanese, who have become experts in the art of preparing a variety of agreeable food products from that refractory soy-bean, which contains such an astonishingly large amount of nutritious proteids, and which, long ago, became for Japan a wholesome, staple article of diet. But the Western races have not yet progressed much beyond the point of preparing cattle-feed and paint oil from the soy-bean, although the more extended culture of this, or similar plants, might work about a revolution in our agricultural economies.

#### AGRICULTURE—A BRANCH OF INDUSTRIAL CHEMISTRY

Agriculture, after all, is nothing but a very important branch of industrial chemistry, although most people seem to ignore the fact that the whole prosperity of agriculture is based on the success of that photochemical reaction which, under the influence of the light of the sun, causes the carbon dioxide of the air to be assimilated by the chlorophyll of the plant.

#### POSSIBILITIES OF PHOTOCHEMISTRY

It is not impossible that photochemistry, which hitherto has busied itself, almost exclusively, within the narrow limits of the art of making photographic images, will, some day, attain a development of usefulness at least as important as all other branches of physical chemistry. In this broader sense, photochemistry seems an inviting subject for the agricultural chemist. The possible rewards in store in this almost virgin field may, in their turn, by that effect of superinduction between industry and science, bring about a rapid development similar to what we have witnessed in the advancement of electricity, as well as chemistry, both of which began to progress by leaps and bounds, far ahead of other sciences, as soon as their growing industrial applications put a high premium on further research. Photochemistry may allow us some day to obtain chemical effects hitherto undreamed of. In general, the action of light in chemical reactions seems incomparably less brutal than all means used heretofore in chemistry. This is the probable secret of the subtle chemical syntheses which happen in plant life. To try to duplicate these delicate reactions of nature by our present methods of high temperatures, electrolysis, strong chemicals and other similar torture-processes, seems like trying to imitate a masterpiece of Gounod by exploding a dynamite cartridge between the strings of a piano.

#### SOME PROBLEMS FOR THE FUTURE

But there are endless other directions for scientific research, relating to industrial applications, which, until now, do not seem to have received sufficient attention.

**RUDIMENTARY CHEMICAL DEVELOPMENT OF THE PETROLEUM INDUSTRY**—For instance, from a chemical standpoint, the richest chemical enterprise of the United States, the petroleum industry, has hitherto chiefly busied itself with a rather primitive treatment of this valuable raw material, and little or no attention has been paid to any methods for transforming at least a part of these hydrocarbons into more ennobled products of commerce than mere fuel or illuminants.

**SYNTHETIC RUBBER**—A hint as to the enormous possibilities which may be in store in that direction, is suggested by the recent work in Germany and England on synthetic rubber; the only factor which prevents extending the laboratory synthesis of rubber into an immense industrial undertaking, is that we have not yet learned how to make cheaply the isoprene or other similar non-saturated hydrocarbons which are the starting point in the process which changes their molecules, by polymerization, into rubber.

**CELLULOSE AND STARCH**—Nor has our science begun to find the best uses for such inexpensive and never exhaustible vegetable products as cellulose or starch. Quite true, several important manufactures, like that of paper, nitrocellulose, glucose, alcohol, vinegar and some others, have been built on it; but to the chemist at least, it seems as if a much greater development is possible in the cheaper and more extended production of artificial fiber. Although we have succeeded in making so-called artificial silk, this article is still very expensive; furthermore, we have not yet produced a cheap, good, artificial fiber of the quality of wool.

**ARTIFICIAL PRODUCTION OF SOLUBLE POTASH-SALTS**—If we have made ourselves independent of Chile for our nitrogen supply, we are still absolutely at the mercy of the Stassfurt mines in Germany for our requirements of soluble potash-salts, which are just as necessary for agriculture. Shall we succeed in utilizing some of the proposed methods for converting that abundant supply of feldspar, or other insoluble potash-bearing rocks, into soluble potash-salts by combining the expensive heat treatment with the production of another material like cement, which would render the cost of fuel less exorbitant? Or shall the problem be solved by setting free soluble potassium salts as a by-product in a reaction engendering other staple products consumed in large quantities?

We have several astonishingly conflicting theories about the constitution of the center of the globe, but we have not yet developed the means to penetrate the world's crust beyond some deep mines—merely an imperceptible faint scratch on the surface—and in the meantime, we keep on guessing, while today astronomers know already more about the surface of the planet Mars than we know about the interior of the globe on which we live.

**INTENSE PRESSURES AND HEAT**—Nor have we learned to develop or utilize the tremendous pressures under which most minerals have been formed, and still less do we possess the means to try these pressures, in conjunction with intensely high temperatures.

No end of work is in store for the research chemist, as well as for the chemical engineer, who can think for himself, without always following the beaten track. We are only at the beginning of our successes, and yet, when we stop to look back to see what has been accomplished during the last generations, that big jump from the rule-of-thumb to applied science is nothing short of marvelous.

#### A RETROSPECT

Whoever is acquainted with the condition of human thought today must find it strange, after all, that scarcely seventy years ago, Mayer met with derision even among the scientists of the time, when he announced to the world that simple but fundamental principle of the conservation of energy.

We can hardly conceive that just about the time the Columbia School of Mines was founded, Liebig was still ridiculing Pasteur's ideas on the intervention of microorganisms in fermentation, which have proved so fecund in the most epoch-making applications in science, medicine, surgery and sanitation, as well as in many industries.

Fortunately, true science, contrary to other human avocations, recognizes nobody as an "authority," and is willing to change her beliefs as often as better studied facts warrant it; this difference has been the most vital cause of her never-ceasing progress.

**PASTEUR'S RUDIMENTARY LABORATORY FACILITIES**—It may astonish the younger generation, surrounded with research laboratories everywhere, to learn that scarcely fifty years ago, that great benefactor of humanity, Pasteur, was still repeating his pathetic pleadings with the French government to give him more suitable quarters than a damp, poorly lighted basement, in which he was compelled to carry on his research; and such was the condition of affairs in no less a place than Paris, the same Paris that was spending, just at that time, endless millions for the building of her new Opera-Palace.

#### REASON FOR AMERICA'S SLOW DEVELOPMENT OF CHEMICAL INDUSTRY

Such facts should not be overlooked by those who might think that America has been too slow in fostering chemical research.

If the United States has not participated as early as some European countries in the development of industrial chemistry, this was chiefly because conditions here were so totally different from those in countries like Germany, England and France, that they did not warrant any such premature efforts. In a country so full of primary resources, agriculture, forests, mines and the more elementary industries directly connected therewith, as well as the problems of transportation, appealed more urgently to American intellectual men of enterprise. Why should anybody here have tried to introduce new difficult or risky chemical industries, when on every side more urgently important fields of enterprise were inviting all men of initiative?

Chemical industries develop along the lines furnished by the most immediate needs of a country. Our sulfuric acid industry, which can boast today of a yearly production of about three million tons, had to begin in an exceedingly humble way, and the first small amounts of sulfuric acid manufactured here found a very scant outlet,

It required the growth of such fields of application as petroleum refining, superphosphates, explosives and others, before the sulfuric acid industry could grow to what it is today.

#### CHEMICAL TRADE BETWEEN THE UNITED STATES AND GERMANY

At present, similar influences are still dominating our chemical industries; they are generally directed to the mass production of partly manufactured articles. This allows us to export, at present, to Germany, chemicals in crude form, but in greater value than the total sum of all the chemical products we are importing from her, although it can not be denied that a considerable part of our imports are products like alizarine, indigo, aniline dyes and similar synthetic products which require higher chemical manufacturing skill. In this connection, it may be pointed out that our exports of oleomargarine to Germany alone, are about equivalent to our imports of aniline dyes.

#### SOME CHEMICAL INDUSTRIES IN WHICH THE UNITED STATES WAS PIONEER

But all this does not alter the fact that in several important chemical industries the United States has been a pioneer. Such flourishing enterprises as those of the artificial abrasives, carborundum and alundum, calcium carbide, aluminum and many others, testify how soon we have learned to avail ourselves of some of our water-power.

One of the most important chemical industries of the world, the sulfite cellulose industry, of which the total annual production amounts to three and a half million tons, was originated and developed by a chemist in Philadelphia, B. C. Tilgman. But its further development was stopped, for awhile on account of the same old trouble, lack of funds, after \$40,000 were spent, until some years later, it was taken up again in Europe and reintroduced in the United States, where it has developed to an annual production of over a million tons.

What has been accomplished in America in chemical enterprises, and what is going on now in industrial research, has been brilliantly set forth by Mr. Arthur D. Little.<sup>1</sup>

#### EARLY BEGINNING OF STUDY OF CHEMISTRY IN THE UNITED STATES

At no time in the history of the United States was chemistry neglected in this country; this has recently been brought to light in the most convincing manner by Professor Edgar F. Smith, of Philadelphia.<sup>2</sup>

The altruistic fervor of that little group of earlier American chemists, who, in 1792, founded the Chemical Society of Philadelphia (probably the very first chemical society in the world), and in 1811, the Columbia Chemical Society of Philadelphia, is best illustrated by an extract of one of the addresses read at their meeting in 1798:

"The only true bases on which the independence of our country can rest are agriculture and manufactures. To the promotion of these nothing tends in a higher degree than chemistry. It is this science which teaches man how to correct the bad qualities of the land he cultivates by a proper application of the various species of manure, and it is by means of a knowledge of this science that he is enabled to pursue the metals through the various forms they put on in the earth, separate them from substances which render them useless, and at length manufacture them into the various forms for use and ornament in which we see them. If such are the effects of chemistry, how much should the wish for its promotion be excited in the breast of every American! It is to a general diffusion of knowledge of this science, next to the virtue of our countrymen, that we are to look for the firm establishment of our independence. And may your endeavors, gentlemen, in this cause, entitle you to the gratitude of your fellow-citizens."

This early scientific spirit has been kept alive throughout the following century by such American chemists as Robert Hare,

<sup>1</sup> THIS JOURNAL, 5 (1913), 793.

<sup>2</sup> "Chemistry in America," published by D. Appleton & Co., New York and London, 1914.



E. N. Horsford, Wolcott Gibbs, Sterry Hunt, Lawrence Smith, Carey Lea, Josiah P. Cooke, John W. Draper, Willard Gibbs and many others still living.

#### PRESENT CONDITIONS OF CHEMISTRY IN AMERICA

Present conditions in America can be measured by the fact that the American Chemical Society alone has over seven thousand members, and the Chemists' Club of New York has more than a thousand members, without counting the more specialized chemical organizations, equally active, such as the American Institute of Chemical Engineers, the American Electrochemical Society and many others. During the later years, chemical research is going on with increasing vigor, more especially in relation to chemical problems presented by enterprises, which, at first sight, seem rather remote from the so-called chemical industry.

#### RESEARCH IN AMERICA

But the most striking symptom of newer times is that some wealthy men of America are rivaling each other in the endowment of scientific research on a scale never undertaken before, and that the scientific departments of our Government are enlarging their scope of usefulness at a rapid rate. But we are merely at the threshold of that new era where we shall learn better to use exact knowledge and efficiency to bring greater happiness and broader opportunities to all. However imposing may appear the institutions founded by the Nobels, the Solvays, the Monds, the Carnegies, the Rockefellers and others, each of them is only a puny effort in comparison with what is bound to come when governments do their full share. For instance, the Rockefeller Institute is spending, to good advantage, about half a million dollars per annum for medical research, but the chewing-gum bill of the United States alone would easily support half a dozen Rockefeller Institutes; and what a mere insignificant little trickle all these research funds amount to, if we have the courage to compare them to that powerful gushing stream of money which yearly drains the war budget of all nations.

In the meantime, the man of science is patient and continues his work steadily, if somewhat slowly, with the means hitherto at his disposal. His patience is inspired by the thought that he is not working for today, but for tomorrow. He is well aware that he is still surrounded by too many "men of yesterday," who delay the results of his work.

#### EFFICIENCY VS. WASTE

Sometimes, however, he may feel discouraged that the very efficiency he has succeeded in reaching at the cost of so many

painstaking efforts, in the economical production of such an article of endlessly possible uses, as Portland Cement, is hopelessly lost many times over and over again, by the inefficiency, waste and graft of middlemen and political contractors, by the time it gets on our public roads, or in our public buildings. Sometimes the chaos of ignorant brutal waste which surrounds him everywhere may try his patience. Then again, he has a vision that he is planting a tree which will blossom for his children and will bear fruit for his grandchildren.

In the meantime, industrial chemistry, like all other applications of science, has gradually called into the world an increasing number of men of newer tendencies, men who bear in mind the future rather than the past, who have acquired the habit of thinking by well-established facts, instead of by words, of aiming at efficiency instead of striking haphazard at ill-defined purposes. Our various engineering schools, our universities, are turning them out in ever-increasing numbers, and better and better prepared for their work. Their very training has fitted them out to become the most broad-minded progressive citizens.

#### PRIVATE GAIN OR PUBLIC SERVICE

However, their sphere of action, until now, seldom goes beyond that of private technical enterprises for private gain. And yet there is not a chemist, not an engineer worthy of the name, who would not prefer efficient, honorable public service, freed from party politics, to a mere money-making job.

But most governments of the world have been run for so long almost exclusively by lawyer-politicians, that we have come to consider this as an unavoidable evil, until sometimes a large experiment of government by engineers, like the Panama Canal, opens our eyes to the fact that, after all, successful government is—first and last—a matter of efficiency, according to the principles of applied science.

Was it not one of our very earliest American chemists, Benjamin Thompson, of Massachusetts, later knighted in Europe as Count Rumford, who put in shape the rather entangled administration of Bavaria by introducing scientific methods of government?

#### APPLIED SCIENCE AND THE DESTINY OF NATIONS

Pasteur was right when one day, exasperated by the politicians who were running his beloved France to ruin, he exclaimed: "In our century, science is the soul of the prosperity of nations and the living source of all progress. Undoubtedly, the tiring daily discussions of politics seem to be our guide. Empty appearances! What really leads us forward are a few scientific discoveries and their applications."

## CURRENT INDUSTRIAL NEWS

By M. L. HAMLIN

### AMMONIUM CHLORIDE, A NEW BY-PRODUCT OF GAS WORKS, ETC.

An article with this title, which appeared recently in the *Chemische Zeitschrift*, 13 (1914), 117, explains why ammonium chloride, particularly, presents certain advantages today over ammonium sulfate as a by-product and describes the general method of manufacture.

Among the reasons for manufacturing the chloride rather than the sulfate, are, *first*, the fact that there is a market for the pure chloride, *second*, the fact that in the condensates from gas manufacture, ammonia is already present to, by far, the greatest extent as the chloride, and *third*, the possibility of an over-supply of ammonium fertilizer salts coming on the market in the future through the further development of synthetic nitrogen fertilizer processes.

In the manufacture of the pure product two chief results must be attained; the ammonia present otherwise than as the

chloride must be transformed, and impurities, chiefly organic, must be removed. For example, the liquor, containing perhaps 200 g. salt per liter, is acidified with hydrochloric acid and oxidized with an air current. Sulfur is filtered off and iron precipitated with ammonia. Ammonium sulfate is decomposed by sodium chloride after filtration and neutralization of excess ammonia, and the solution is evaporated to dryness. The residue is now sublimed, the ammonium chloride being thus separated from sodium sulfate and chloride, a small amount of phosphates and most of the organic impurities.

Three fractions are collected in different parts of the apparatus: 1—The residue consists chiefly of sodium chloride, sodium sulfate and finely divided carbon. 2—On the cover of the apparatus is deposited pure ammonium chloride. 3—In the helmet is found a small amount of the salt contaminated with organic impurities. Fraction 2 includes 90–95 per cent of the salt present; while it is analytically pure, traces of organic substances

are present in sufficient amount to discolor it, and a recrystallization is necessary in order to obtain a pure white product of the highest grade.

The method is patented and is controlled and being applied by the Berlin-Anhaltische Maschinenbau Aktien-Gesellschaft.

### STOCKHOLM GAS-WORKS IN 1913

The gas production of the Stockholm Gas-Works in 1913 was 44,720,880 cubic meters (about 1580 million cubic feet)—an increase of 7.54 per cent on the previous year. The average gross calorific value was 5150 calories (579 B. T. U.). There were carbonized 137,185 metric tons of coal, 11,500 cubic feet of gas being produced per ton. The gas consumption amounted to 44,649,180 cubic meters, or 7.34 per cent higher than in 1912. Of the whole amount, 9.96 per cent was used for public lighting, 84.94 per cent sold to consumers, 1.81 per cent used on the works, and 3.29 per cent unaccounted for. The consumption per head of the population was 123.8 cubic meters (4372 cubic feet). The meters in use increased by 4609 to 80,602, of which 32.74 per cent were prepayment. The number of flat-flame burners in use was 36,425, and incandescents 106,928. These data appear in the *Jour. Gas Lighting and Water Sup.*, 127 (1914), 110, which goes on to say that satisfactory increases were shown in all domestic gas-consuming apparatus, and gas-engines decreased in number, while increasing considerably in horsepower. The price of gas is about \$0.75 per 1000 cubic feet, with discounts of 5 and 10 per cent for larger consumers.

### CARBON MONOXIDE AND NITRIC OXIDE FROM HEATING AND LIGHTING BURNERS

The *Journal für Gasbeleuchtung* for the 27th of June and the 11th of July contained a communication by Dr. E. Terres on researches which he has carried out, with collaborators, at the Chemical-Technical Institute of the Technical College at Karlsruhe. He has investigated the proportion of carbon monoxide and nitric oxide in the gas-flames of both lighting and heating burners, with the object of throwing further light on the hygiene of flame methods of lighting.

The products of combustion examined included those from both inverted and upright incandescent gas-burners, the petroleum lamp and the candle, and heating gas-burners. The work on the inverted burner is especially interesting, as it has not hitherto been investigated from this standpoint. The general conclusions at which the author arrives are:

1—All flames give a very trifling proportion of carbon monoxide of approximately the same order as to quantity in all cases, viz., 0.002 to 0.004 volume of carbon monoxide per volume of carbonic acid. With insufficiency of primary air, this figure may rise to 0.017 to 0.020 volume.

2—All flames likewise give a quite uniform, but quite trifling, proportion of nitric oxide, viz., 0.0006 to 0.0017 volume of nitric oxide per volume of carbonic acid.

3—The products of combustion with town gas containing the usual quantity of sulfur will have 0.00025 to 0.0012 volume of sulfur dioxide per volume of carbonic acid.

The concentration of all these gases, even if the carbonic acid reaches 1 per cent by volume of the air, is, therefore, far below the limit which authorities on hygiene regard as likely to be injurious to health. Experiments in a room of 1700 cubic feet capacity without special ventilation showed that, owing to natural ventilation, a proportion of 0.5 to 0.75 per cent of carbonic acid could only rarely be attained in a dwelling-room lighted by gas.

### OIL IN AUSTRALIA

Considerable attention is being paid to prospecting for oil deposits in South Australia, and to radioactive ores. Licenses

to search for oil have been granted, and bores are being put down in the southern part of Kangaroo Island, the southwest of Eyre Peninsula and in the southeast. [*Engineering* (London), 98 (1914), 71.] The Government has offered a bonus of \$20,000 for the first 100,000 gallons of crude petroleum containing not less than 90 per cent of products obtainable by distillation.

### CANADIAN COAL

According to *Engineering* (London), 98 (1914), 64, the coal of the Bellz River formation and the Edmonton formation in Canada grades between lignites and bituminous. The coal which belongs to the Bellz River horizon is found over an area of about 25,000 square miles; of this area 5000 square miles are estimated to contain 13,000,000,000 tons of coal. The amounts of coal contained in the two provinces of Alberta and Saskatchewan have been estimated at 10,000,000,000 tons and 3,000,000,000 tons, respectively. The principal coal-mines within this area in Alberta are near Lethbridge, Taber and Lund Creek. The coal of the Edmonton formation is generally lignites, but in the foothills it grades up to bituminous. The total area of workable coal has been estimated at 12,800 square miles, with a probable coal content of 71,000,000,000 tons. The principal coal-mines within this area are near Edmonton. The coal-fields of Saskatchewan are situated in the southern portion of the province, and extend from the boundary of Alberta on the west to the Manitoba boundary on the east. The area underlain by coal is estimated at 5,500 square miles, containing in all about 18,000,000,000 tons of lignite.

### BRITISH COAL EXPORTS IN THE FIRST HALF OF 1914

The exports of coal from the United Kingdom in the first half of this year—the expression “coal” including coke and patent fuel—amounted to 36,146,907 tons, and when to this is added coal shipped for the use of steamers engaged in foreign trade, the aggregate for six months becomes 46,329,064 tons. [*Engineering* (London), 98 (1914), 123.] Coal has accordingly been leaving England this year at the rate of 92,658,128 tons per annum. The corresponding movement in the corresponding period of 1913 was at the rate of 94,270,348 tons per annum, and in the corresponding period of 1912 at the rate of 70,445,222 tons per annum. The principal exports to June 30, this year, were: Russia, 2,009,789 tons; Sweden, 1,800,093 tons; Norway, 1,247,501 tons; Denmark, 1,389,551 tons; Germany, 4,202,651 tons; France, 6,818,125 tons; Spain, 1,756,681 tons; Italy, 4,533,077 tons; Egypt, 1,636,842 tons; and the Argentine Republic, 1,825,940 tons.

### THE ALTIOR PROCESS OF DIE-CASTING

The National Alloys, Limited, Ilford, London, E., have recently brought out an improved process of die-casting for aluminum alloys, which possesses several interesting features. It is described in a recent issue of *Engineering* (London) 98 (1914), 131. The process is for use with aluminum alloys of a specific gravity of 2.85. The alloy recommended is ivanium, which has a tensile strength of 12 tons, and 6 per cent elongation on 2 in. This alloy is guaranteed not to disintegrate, and it is not affected by sea-water, etc. The casting machine has a gas-heated melting-pot lined with refractory material and provided with a cover. Extending from the cover to within a short distance of the bottom of the pot is a tube of refractory material connecting with a neck-piece fixed above the cover and surrounded by a burner. Above this neck-piece is fixed a plate, to which the bottom half of the die is fastened. The plate, which is hinged and can be thrown back by a worm and spur-gear, also carries the standards and cross-frame for a large vertical quick-pitch screw, to which the upper part of the die is fastened. Between the lower die-plate and the neck is a

slot, in which works a sprue-cutting bar. The action is as follows: after fixing the dies the sprue-cutting bar of hardened steel is pushed over, so that communication between the inside of the pot and the die is prevented. An inert gas is then admitted to the pot above the metal, and a high pressure maintained inside the pot. When the metal is melted and the sprue-cutter pulled over so as to bring a hole in it fair with the hole communicating with the die, metal is forced out of the pot up the tube and neck into the die. The cutter-bar is then pushed over, cutting off the connection, and the upper half of the die raised by the quick-pitch screw. The casting is removed automatically, and the die is returned to its original position. The piece of alloy is punched out of the cutter-bar, and on pulling the bar over again a fresh supply of metal is forced into the die. It is claimed for the machine that the metal is kept hot right up to the time of entering the die, while the dies themselves, being mounted on the pot, are also always kept at a suitable temperature. The whole cover with the die-frame may be swung back, if necessary, by bevel and worm gears. The pot is provided with plungers for mixing the metal and with a filling-hole, while it is surrounded by a casing of refractory material.

#### A NEW BEARING METAL

An account of a new alloy for bearings appears in *The Engineer* for July 3, 1914. It is composed of 65 parts of copper, 30 of lead and 5 of tin. It was tested on the bearings of a tender of a Pacific type locomotive for 50,000 miles, after which it showed a wear of  $\frac{1}{32}$  inch, while the other bearings, of white metal, had to be renewed six times. In other applications it proved twice as durable as phosphor bronze.

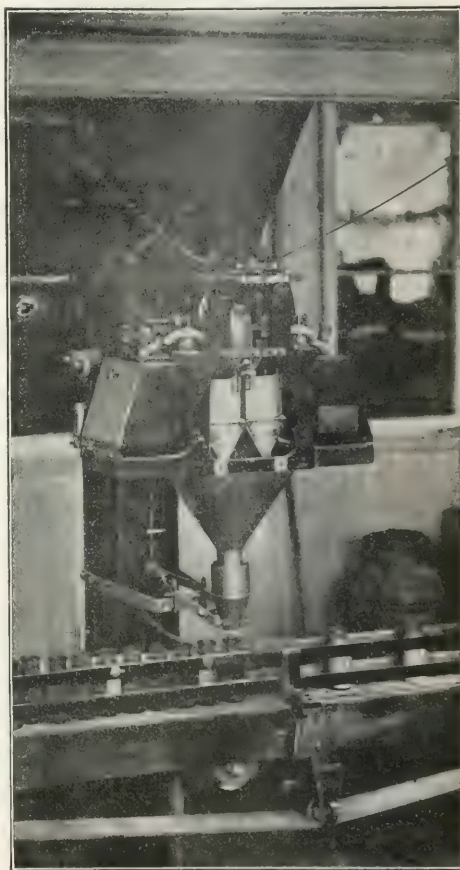
#### ENGLISH TRADE UNIONS IN 1912

The Chief Registrar of Friendly Societies (Great Britain) has issued his Report on Trade Unions for the year ending December 31, 1912, statistics from which are quoted in *Engineering* (London), 98 (1914), 119. During the year 1912 thirty-nine unions were added to, and thirty-six were removed from, the register; of these latter, twenty-three furnished notices of dissolution, eight were amalgamated with other unions, and in five cases the certificate of registry was canceled at the request of the unions. There accordingly remained on the register on December 31, 1912, 683 unions, of which 576 were registered in England and Wales, thirty-one in Scotland, and seventy-six in Ireland. The 683 unions in question had a membership of 2,597,772. In 1903 the unions numbered 742, with a membership of 1,575,375; these figures show a decrease of fifty-nine unions, and an increase of over one million in membership. Among the unions showing the largest increase in membership during the year 1912 we may mention the National Amalgamated Union of Shop Assistants, Warehousemen, and Clerks, with an increase of 42,694; the Amalgamated Society of Engineers, 22,529; the Amalgamated Society of Railway Servants, 15,486; and the Amalgamated Society of Carpenters and Joiners, 12,600. On the other hand, three unions showed a decrease in membership, as follows: The London Carmen's Trade Union, a decrease of 18,405; the Dock, Wharf, Riverside, and General Worker Union, 14,771; and the Lancashire and Cheshire Miners' Federation, 9326. Taking the unions having the largest membership in the year under review (1912), we find the Amalgamated Society of Engineers with 143,998 members; the Durham Miners' Association with 136,966; the Amalgamated Society of Railway Servants of England, Ireland, Scotland, and Wales, with 132,002; the South Wales Miners' Federation with 114,208; the Yorkshire Miners' Association with 99,632; and the National Union of Gas-Workers and General Laborers with 82,135. The total income of the unions in 1912 was, in round numbers, about \$19,000,000, 90.4 per cent of which was contributed by the members, 4 per cent by other trade unions, the remainder, 5.6

per cent being interest on invested funds and contributions from other sources. The average contribution per week received from each member was \$1.54. The total funds of the unions on December 31, 1912 was about \$28,000,000, showing a decrease of approximately \$3,500,000 during the year; this decrease in funds was due to the coal strike, and applied mostly to the funds of the mining group of unions. Taking the six unions at the top of the list, we find that, in round numbers, on December 31, 1912, the Amalgamated Society of Engineers had total funds to the amount of \$3,900,000; the Amalgamated Association of Operative Cotton-Spinners, \$2,000,000; the Amalgamated Society of Railway Servants, \$1,890,000; the Derbyshire Miners' Association, \$1,200,000; The United Society of Boiler-Makers, \$1,200,000; and the Associated Society of Locomotive Engineers, \$840,000.

#### AUTOMATIC EQUIPMENT FOR PLACING POWDERS IN BOTTLES ON NET WEIGHT BASIS

The accompanying illustration shows modern methods for placing hepatic, bromo and other saline preparations of a pow-



dery nature in bottles. Net weight legislation covering drug and food products has made imperative measures necessary, and to accomplish the desired accuracy in handling a large out-



put, special automatic apparatus is now being installed in several laboratories. Empty bottles are conveyed to weighing device where each bottle is held until prescribed amount is placed in container and while in this position a shaking process takes place also which settles material into bottle, when same is released and passes down to corking table for stopper. Net weight discharges are placed in bottles at the rate of 25 per minute. These methods insure a strictly sanitary output. The lay-out as shown is furnished by the Automatic Weighing Machine Company, Newark, N. J.

#### DECREASED ACTIVITY IN ENGLISH SHIPBUILDING

It is interesting to note, in connection with industrial conditions in England, that a falling off of activity in ship building is reported. *Engineering* (London) gives the following statistics [98 (1914), 94] taken from Lloyd's returns, just issued: Including merchant and war ships, there are in course of construction at the present time 567 vessels, aggregating 2,314,669 tons. This is 8.8 per cent less than at the same date last year, notwithstanding that there is an increase in the number of warships now being built. The figures of work now in progress, with those of a year ago, are given in the accompanying table:

	July, 1914		July, 1913		Increase or decrease Per cent
	No.	Tons	No.	Tons	
Merchant ships .....	477	1,722,124	543	2,003,241	-14
H. M. S. (private yards)....	60	306,030	57	273,149	+12
Foreign warships (private yards).....	16	152,145	17	129,300	+17.6
	553	2,180,299	617	2,405,690	-9.4
H. M. S. (dockyards).....	14	134,370	14	132,190	+1.5
	567	2,314,669	631	2,537,880	-8.8

#### AMERICAN RAILROADS

The railroads of the United States, with annual traffic revenues exceeding \$100,000, comprised 242,657 miles of line last year, as compared with 238,220 miles in 1912 according to figures in *Engineering* (London), 98 (1914), 123. The traffic receipts in 1913 were \$3,125,135,000 as compared with \$2,826,958,000 in 1912. The working expenses in 1913 were \$2,169,968,000, as compared with \$1,959,094,000 in 1912. The number of passengers carried last year was 1,033,679,000, as compared with 994,372,000 in 1912. The quantity of freight carried was 2,058,035,000 tons, as compared with 1,818,795,000 tons. The number of locomotives owned was 63,375, as compared with 61,276; and the number of cars was 2,445,508, as compared with 2,368,942. The aggregate number of persons employed upon the lines last year was 1,815,239, as compared with 1,799,931. The average rate of dividend last year upon outstanding stocks was 4.28 per cent.

#### STEAM POWER USED FOR GENERATION OF ELECTRIC CURRENT IN PRUSSIA

According to recent statistics, there were employed for the generation of electric current in Prussia steam engines, portable and stationary, with a capacity of 1,410,000 horse-power, and steam turbines used for the same purpose of 1,160,000 horse-power. As the total registered capacity of steam turbines amounts to 1,240,000 horse-power, it will appear that 95 per cent of the aggregate is used in the generation of electric energy. Altogether, 2,570,000 horse-power of steam power are thus employed in the generating of electricity, and although it is a very substantial figure, it must be looked upon as minimum, inasmuch as many steam engines used for this purpose are not included in the record. [*Engineering* (London), 98 (1914), 44.] In addition to the above, it must be remembered that a vast number of gas and oil engines are used for the same purpose, in addition

to water power; but of these there is no record. The largest total capacity of steam power used for generation of electric current is in the Arnberg district with 389,898 horse-power, and the Düsseldorf district with an aggregate of 419,051 horse-power. Berlin-Potsdam comes next with 375,889 horse-power.

#### DIESEL ENGINES IN THE ITALIAN NAVY

The continuously increasing use of internal combustion engines of the Diesel type is shown by the news, appearing in the *Zeitschr. d. Verein deutscher Ing.*, 58 (1914), 1187, that the new Italian battleship "Cristoforo Colombo" is to have its amidships propeller driven by such an engine. This vessel has 26,000 tons displacement and is fitted with eight heavy guns in four turrets and sixteen smaller guns. She has three screws, one of which, as mentioned, is to be driven by a Diesel engine and is to be used for cruising; the other two are to be driven by Parsons turbines. Oil fuel exclusively is to be used. The speed will be twenty-five knots.

Two small torpedo boats of 120 tons each are also being built to be driven by Diesel engines of 2,900 horse-power. They are expected to develop 32 knots.

#### CALCIUM CARBIDE, CYANAMIDE AND NITRATE

According to a French authority quoted by the *American Machinist*, the world's output of calcium carbide last year exceeded 350,000 metric tons. The autogenous welding of metals requires a large quantity—about 22,000 tons being consumed for this purpose in Germany, as compared with 28,000 tons for illuminating. The price for calcium carbide in Europe was maintained at about \$55 per ton. The production and price are regulated by a Syndicate, which at the end of 1913 was renewed for another term. The production of calcium cyanamide in 1913 was over 150,000 tons. The Odda works in Sweden have a plant capable of making 90,000 tons per annum. The production of calcium nitrate in Europe is between 100,000 and 120,000 metric tons.

#### MINERAL-WATER PRODUCTION IN 1912

Although nearly 58,000,000 gallons of mineral water were bottled and sold in 1913, valued at over \$5,600,000, these figures represent a decrease of 7 per cent in quantity and 15 per cent in value compared with 1912. The decrease in production of mineral waters, which began in 1911, is believed by R. B. Dole, of the United States Geological Survey, to be traceable to the decrease in demand for bottled spring waters consequent on improvements in municipal waterworks. Detailed examination of the statistics for the last few years shows that the installation of municipal purification plants in several large cities has been followed by a marked decrease in the sale of spring waters in the immediate vicinity, and doubtless improvement in the quality of water supplies in smaller municipalities throughout the country has similarly affected the mineral-water business and has contributed to the present lowered production. There is also a tendency toward a lower price, which is caused by decreased sales of high-priced medicinal waters and increased sales of low-priced table waters. The general tendency toward a decline in price is doubtless due to the demand for good, pure, potable bottled waters at moderate cost in place of the former demand for waters reputed to possess exceptional curative properties and therefore commanding fancy prices.

The radioactivity of mineral waters has attracted so much popular attention during the last few years that the Geological Survey's report on mineral waters this year includes a brief discussion by Mr. Dole on the therapeutic value of radioactive waters and the radioactive strength of many well-known springs.

## NOTES AND CORRESPONDENCE

### OBITUARY—RUSSELL S. PENNIMAN

Russell S. Penniman, one of the pioneers of the dynamite industry in the United States, died of acute heart disease at his home in Berkeley, California, on June 17, 1914.

Mr. Penniman was born in Columbus, Ohio, and had just passed his 61st birthday. He entered into the manufacture of nitroglycerine at Hoosac Tunnel, in 1879, and for the thirty-five years following was actively interested in the manufacture of dynamite and allied products. The early years of his life were spent in Massachusetts, and later he resided in Dover, N. J. At the time of his retirement, in 1908, he was general manager of the west coast division of the E. I. du Pont de Nemours Powder Company, with factories on the bay shore. Since 1908, Mr. Penniman was identified with various California enterprises, being president of the West Coast Kalsomine Co. and a director of the First National Bank of Berkeley.

Mr. Penniman was a member of the American Chemical Society, the Chemists' Club and other scientific organizations.

### THE STABILITY OF RESIN ACIDS AT SLIGHTLY ELEVATED TEMPERATURES—A CORRECTION<sup>1</sup>

Schwalbe,<sup>2</sup> noting the evolution of carbon dioxide when rosin was heated to 140° C. in air freed from carbon dioxide, interpreted this result as the breaking down of the carboxyl groups of the acids contained in the rosin.

Herty and Dickson<sup>3</sup> showed that the carbon dioxide obtained by Schwalbe was due to one or more of the following factors: traces of spirits of turpentine in the rosin, moisture, oxygen of the air conducted through the heating flask and oxygen absorbed by the rosin previous to the experiment. Rosin, prepared from fresh oleoresin, freed completely from spirits of turpentine during distillation, and heated in a current of dry nitrogen, showed no signs of decomposition at 140°, even after seven hours' heating at this temperature.

But they further stated that if the resin acids were prepared cold and freed from the other constituents of the fresh oleoresin, such acids heated in dry nitrogen melted at 65°–70° C. and immediately evolved carbon dioxide in quantity. No explanation was offered of this seeming paradox, the results, however, indicating a probable decomposition of some of the acid constituents of the oleoresin during its separation by distillation, in the woods, into rosin and spirits of turpentine.

Later, in seeking an explanation, two possibilities suggested themselves: *First*, that during the preparation of the acids some oxygen might have been absorbed from the air, in spite of the precautions taken; *second*, that the drying of the acids in a desiccator over phosphorus pentoxide may have been imperfect. This last idea was suggested during the course of another investigation in this laboratory, in which great difficulty was experienced in drying perfectly resin acids precipitated from water solutions of their potassium salts by acidifying with hydrochloric acid.

To test these ideas, a perfectly fresh specimen of the oleoresin of *Pinus heterophylla* (Cuban or slash pine) was obtained from Florida. Five grams of this specimen were dissolved in 50 cc. of ether, the solution filtered and the potassium salts of the acids immediately precipitated by slowly adding 10 cc. of a very concentrated water solution of potassium hydroxide, approximately 15 normal, a salting-out process. This precipitate, freed as far as possible from the potassium hydroxide solution by draining, was thoroughly mixed with glass wool to make the

mass more permeable to the extractive, and extracted with ether one hundred hours in a Soxhlet extractor until no further traces of spirits of turpentine or resene could be detected in the fresh extract. The extracted mass was treated with cold water and the solution of the potassium salts filtered from the glass wool. The free acids were precipitated by slow addition of dilute hydrochloric acid, just to acidity, filtered upon a Buchner funnel, washed with water until free from chlorides, and rapidly dried as far as possible with the suction pump. The partly dried acids were dissolved in ether and the removal of water completed by addition of freshly ignited sodium sulfate. This solution was rapidly filtered into the heating flask in which the experiment was to be conducted.

This flask had been previously filled with nitrogen obtained by drawing air successively through a water solution of ammonia; over heated copper; through dilute sulfuric acid; two wash bottles containing alkaline pyrogallol acid solution; concentrated sulfuric acid and two drying tubes—one containing calcium chloride and soda lime, the other phosphorus pentoxide mixed with pumice. The heating flask, surrounded by a bath of cottonseed oil in a beaker, contained a thermometer, and its outlet tube, during the heating experiment, dipped below the surface of freshly filtered barium hydroxide solution in the precipitating flask. A tube of soda-lime was placed between the precipitating flask and the aspirator.

The ether solution of the resin acids was evaporated to dryness in the heating flask in a current of dry nitrogen under reduced pressure, barium hydroxide solution was then filtered into the precipitating flask and the temperature of the heating flask slowly raised, nitrogen being drawn through the flask throughout the experiment.

The acids melted at about 73° C., but no gas evolution could be detected in the melted mass, even while the temperature was being raised to 140° C. and so maintained for an hour, nor was there the slightest precipitation of barium carbonate in the precipitating flask. It is evident, therefore, that these resin acids, if protected from oxygen and thoroughly freed from water, are perfectly stable at 140° C.

CHAS. H. HERTY and H. L. COX

UNIVERSITY OF NORTH CAROLINA  
CHAPEL HILL, N. C.

### EXHIBITION MINE AT THE PANAMA-PACIFIC EXPOSITION

The plans for the mine beneath the floor of the Palace of Mines and Metallurgy at the Panama-Pacific Exposition, San Francisco, have now progressed under the direction of the Bureau of Mines to the point where it is expected that a comprehensive exhibit of mines and mining subjects, including mining equipment and supplies, will be presented.

Characteristic working places, or stopes, will be prepared in the mine to simulate the character of the ore, or coal; and the methods of working—typical of some of the largest and most important copper, silver, lead, gold, and anthracite and bituminous coal mines of the country—and motion pictures will be shown in one of the rooms of the mine, illustrative of workings such as open-cut copper and iron mines and stone quarries, which cannot otherwise be shown in such an exhibit.

The entrance to the mine may be made by a shaft or by a slope which is located adjacent to the Bureau of Mines space in the Government exhibit. From the bottom of the shaft, which is on a lower level, the entry way leads past small rooms which will be used for exhibits of lamps, mining journals, etc., through metal mining stopes, showing two levels in which various mining machines will be shown as working exhibits. Beyond the

<sup>1</sup> Presented at the 49th Meeting of the American Chemical Society, Cincinnati, April 6–10, 1914.

<sup>2</sup> *Zeit. anorg. Chem.*, **18**, 1852

<sup>3</sup> *This Journal*, **1**, 148.

metal mining rooms the entry leads past a room typical of the Pennsylvania anthracite mines and a room typical of the Pacific Coast coal mines, in which the sloping veins occur. At this point steps in the entry lead to an upper level, along which are arranged rooms of bituminous coal mines.

The mine will be equipped with the usual tracks, trolleys, locomotives, cars, cages, hoists, motors, pumps, air compressor drills, mining machines, signs, mine doors, etc., all of which will be installed as working exhibits.

Each day there will be a demonstration of rescue and first-aid following an imaginary explosion in the mine. Rescue crews from the Bureau of Mines exhibit will enter the mine wearing apparatus and bring out the supposed victims, who will be given first-aid treatment in the surface emergency hospital, which will be one of the features of the Bureau's exhibit.

The exhibit should serve a good purpose in educating the public regarding the magnitude of the mining industry, the cost of its operation, and the amount of capital invested in its conduct.

## INDUSTRIAL ACCIDENTS IN PENNSYLVANIA IN 1912

The fatal and non-fatal accidents occurring in the various industries of the State of Pennsylvania during the year 1912 have recently become available. These may be summarized as follows:

CASUALTIES					
INDUSTRY	No. of employees	TOTAL		FATAL	
		No.	Per cent of employees	No.	Per cent of employees
Anthracite coal.....	172,868	4,105	2.4	521	12.7
Bituminous coal.....	172,646	7,416	4.3	462	6.2
Iron and steel.....	136,966	33,742	24.6	215	0.6
Locomotives.....	29,119	4,948	17.0	19	0.4
Glass.....	26,411	969	3.7	6	0.6
Cars and car wheels.....	20,242	2,436	12.0	16	0.7
Pig iron.....	14,560	5,269	36.2	16	0.3
Tin plate.....	10,477	134	1.3	1	0.7
Cement.....	8,867	1,156	13.0	19	1.6
Paper.....	7,765	647	8.3	14	2.2
Tanning.....	6,527	296	4.5	5	1.7
Petroleum.....	6,532	75	1.1	5	6.7
Chemical.....	5,852	96	1.6	3	3.1

W. A. HAMOR

## PERSONAL NOTES

The new million dollar by-product coke plant of the Maryland Steel Co. at Sparrows Point, Md., was put in operation on July 22nd. It consists of two batteries of 60 ovens each and is of the Koppers type.

Bertram O. Beckett, for 34 years identified with the Whittall-Tatum Co., of Millville, N. J., has withdrawn from the firm to accept the superintendency of the Cumberland and More-Jonas Glass Works, at Bridgeton, N. J., and the Minotola Glass Works, at Minotola, N. J.

Litigation over the Macbeth-Evans Glass Company's "Alba" glass formula has been settled out of court; the firms involved have reached an amicable agreement with the Macbeth-Evans Company and are now using the formula on a royalty basis.

Professor Francis Humphreys Storrer, professor of chemistry in the Massachusetts Institute of Technology from 1865 to 1870 and professor of agricultural chemistry at Harvard University from 1870 to 1907, when he retired as emeritus professor, died at his home in Boston, July 31st, at the age of 82 years.

The window glass factories at Sandusky, Ohio, formerly operated by the Enterprise Glass Co., and later by the Republic Glass Co., of which Myron L. Case is the head, have been leased to the Pittsburgh Plate Glass Co., by which both will be operated, one with the use of mechanical blowers, the other by hand workmen. Mr. George Moore, formerly with the American Window Glass Co., at Arnold, Pa., is to supervise operations at both factories.

The Macbeth-Evans Glass Co. has installed in the National Museum at Washington, D. C., a small glass plant showing the manufacture of glassware from the raw materials to the finished product. The exhibit was prepared under the personal supervision of Mr. George A. Macbeth and was a gift to the Museum.

Dr. Frederic Lawrence Kortright, instructor in chemistry at Cornell University from 1892 to 1899 and subsequently assistant professor and professor of chemistry at the University of West Virginia, died on July 13th, at the age of forty-seven years.

Work on building the new benzol plant at the works of the Carnegie Steel Co., Farrell, Pa., was started during the middle of August. This plant will cost between \$400,000 and \$500,000.

Mr. Frederick Soddy, lecturer in physical chemistry in the University of Glasgow, has been appointed to the chair of chemistry at the University of Aberdeen, in succession to Professor F. R. Japp.

The McKeesport Tin Plate Co., is preparing plans for 18 new mills at its Port Vue, Pa., works. This Company has at present 22 mills.

The American Tar Products Co., of Chicago, Ill., has let a contract for the construction of a \$100,000 plant to manufacture tar products from the tar output of the Woodward Iron Company's coke ovens.

The DeLaval Separator Co. maintain an Experimental Creamery at their Poughkeepsie, N. Y. works. The equipment includes modern machinery and the necessary apparatus for making chemical and bacteriological examinations of all dairy products.

The National Window Glass Manufacturers' Association elected the following officers at the closing session of its annual convention at Atlantic City, July 24: *President*, O. C. Teague, Utica, Ohio; *Vice-President*, J. H. Brewster, Weston, W. Va.; and *Secretary*, J. K. Johnson, Pittsburgh, Pa.

The past operating year was one of the worst that the flint glass workers of this country have experienced in more than a decade. The factories, as a general rule, operated only from 50 to 75 per cent of their capacity.

Prof. John C. Olsen, formerly professor of analytical chemistry at the Polytechnic Institute, Brooklyn, has accepted a position at Cooper Union, New York, as professor of chemistry and head of the department of chemistry.

The Whittall-Tatum Co., of Millville, N. J., have under erection a machine shop, in the construction of which some \$30,000 will be expended. This shop is to take care of an increased demand for machines and presses.

Mr. Roger L. Morrison, highway engineer with the United Gas Improvement Co. of Philadelphia, has been appointed professor of highway engineering in the Agricultural and Mechanical College of Texas. Mr. Morrison received the degree of Master of Arts from Columbia University in June, having completed the graduate course in highway engineering.

Nokomis Lodge, the elaborate summer home of W. H. Nichols of the General Chemical Company of New York, and the outlying buildings were destroyed on the afternoon of July 20th. The house, one of the largest on the St. Lawrence River, was situated on Wolf Island, in the Canadian Channel. The fire started in the kitchen. The steam yacht Nokomis was cut adrift and floated down the stream unharmed. Only a few small articles were saved from the fire.



# GOVERNMENT PUBLICATIONS

By R. S. MCBRIDE, Bureau of Standards, Washington

**NOTICE**—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate. Consular Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington. The regular subscription rate for these Consular Reports mailed daily is \$2.50 per year, payable in advance; to the Superintendent of Documents.

## BUREAU OF STANDARDS

**Combustion Method for the Direct Determination of Rubber.** L. G. WESSON. Technologic Paper 35. 11 pp. This article was published practically in full in *THIS JOURNAL*, 6 (1914), 459-62.

**Iodine Number of Linseed and Petroleum Oils.** W. H. SMITH and J. B. TUTTLE. Technologic Paper 37. 17 pp. An experimental investigation of the Hanus method for determination of iodine number of oils shows that this procedure should be more exactly defined in order to give reproducible results, particularly with burnt oils. The effect of weight of sample, temperature, time of absorption and amount of Hanus solution were investigated.

**Observations on Furnishing Temperature and Properties of Rails.** G. K. BURGESS, J. J. CROWE, H. S. RAWDON and R. G. WALTEMBERG. Technologic Paper 38. 63 pp. This is the first report of a series which will be prepared in connection with the metallurgical and metallographic investigations by the Bureau of Standards in connection with rail specifications. The importance of rolling rails at proper temperature is well known, but the specifications limiting the shrinkage to 6.75 in. in 33 ft. have been found to be of no importance commercially since this clause does not serve its avowed purpose of limiting the finishing temperature to a value slightly above the critical range. In this paper data are given which have been collected from investigations in four representative mills and some experimental work in the Bureau laboratories. It is concluded that a comparison of chemical analyses, microphotographic examination and physical properties of finished rails, the rolling of which was observed, does not afford sufficient evidence of co-relation to warrant associating any of the properties either with the temperature of rolling or with each other. Data are given for the thermal expansion of various steels and the commercial significance of the shrinkage specifications is pointed out.

## GEOLOGICAL SURVEY

The following data, taken from advanced chapters of mineral resources for 1913, are of particular interest at this time as showing relative American production of metals and mineral products and indicating the possible influence of the interruptions of foreign commerce at this time.

**Recovery of Secondary Metals.** J. B. DUNLOP. Separate No. 5 from Vol. 1. 8 pp. Secondary metals are defined as "those recovered from scrap metal, sweepings, skimmings, drosses, etc., and are so called to distinguish them from the metals derived from ore, which are termed 'primary metals.' This distinction does not imply that secondary metals are of inferior quality." The importance of the industries for reclaimed metal is brought out by the following table, which shows the quantity and value of secondary metals produced in 1913:

RECOVERY OF SECONDARY METALS IN THE U. S. IN 1913

Metal	Quantity (Short tons)	Value Dollars
Secondary copper, including that in alloys	66,980	20,536,068
other than brass.....	99,315	24,651,969
Remelted brass.....	33,104	6,409,392
Secondary lead.....	50,005	6,019,776
Recovered lead in alloys.....	6,415	12,567,379
Secondary spelter.....	3,743	450,932
Recovered zinc in alloys other than brass.....	7,763	2,199,480
Secondary tin.....	45	72,844,996
Recovered tin in alloys.....	2,660	
Secondary antimony.....	2,198	
Recovered antimony in alloys.....	2,456	
Secondary aluminum.....		
Recovered aluminum in alloys.....		
Total.....		

**The Production of Graphite in 1913.** EDSON S. BASTIN. Separate No. 14 of Vol. 2. 72 pp. "In the present report there is republished in full or in abstract all of the information on graphite that has appeared in previous survey reports. This information has been amplified in some parts and brought up to date whenever possible. It will be unnecessary, therefore, for readers to refer to any earlier survey report dealing with this mineral."

The article covers the following subjects: Physical and chemical characteristics, origin, uses, production, and imports; and full summaries are given, by geographical sources, of the various graphite-producing districts both of this and foreign countries. The bibliography includes the more important articles of mineralogical and economic interest.

It is pointed out that the production of graphite in the United States is very irregular and at the present time only one concern is said to be firmly established "in the treatment of such graphite rocks." The production in the United States in 1913 was 4,775 short tons of natural graphite valued at \$293,000 and 6,817 short tons of manufactured graphite valued at \$973,000. There were imported 288,791 short tons valued at \$2,109,000. The three causes for the unsatisfactory condition of the domestic industry are given as follows: "(1) The superiority of much of the Ceylon graphite to any graphite that is mined in this country; (2) the low cost of labor in Ceylon, which permits cheap mining, careful sorting, rubbing up, and blending of the product; and (3) the facts that the largest domestic deposits are schists which carry small flakes of graphite disseminating throughout them and the separation of graphite from the accompanying minerals, especially mica, in such rocks is a problem of unusual difficulty."

**The Production of Abrasive Materials.** FRANK J. KATZ. Separate No. 15 from Vol. 2. 22 pp. This report gives detailed information as to the production in this country and abroad of the various abrasives. Details are given for the following: Millstones, grindstones, oilstones, corundum and emery, abrasive garnet, tripoli and diatomaceous earth, pumice, and artificial abrasives. The importance of these industries is shown by the following tabulation of abrasives consumed in the United States in 1913, exclusive of the various forms of silica and feldspar:

Natural abrasives.....	\$1,648,578
Artificial.....	2,017,458
Imports.....	916,913
Total.....	4,582,949

**The Production of Phosphate Rock in 1913.** W. C. PHALEN. Separate No. 16 of Vol. 2. 20 pp. The marketed production of phosphate rock in the United States in 1913 was 3,111,221 long tons, valued at nearly \$12,000,000. This was an increase of 5 per cent in quantity and 1 per cent in value over the previous year. Five-sixths of all the material came from Florida. The range in prices per ton was \$3.20 to \$6.10, averaging \$3.79.

Other data included in this report which are of particular interest to the fertilizer industry are the following:

**FERTILIZERS IMPORTED AND ENTERED FOR CONSUMPTION IN THE U. S. IN 1913**

Product	Quantity Long tons	Value Dollars
Apatite.....	2,962	22,471
Bone dust or animal carbon, and bone ash, fit only for fertilizing purposes.....	35,012	851,136
Calcium cyanamid or lime nitrogen.....	26,729	1,410,248
Guano.....	16,674	518,429
Kainit.....	465,336	2,201,730
Manure salts, including double manure salts.....	223,687	2,245,509
Phosphates, crude.....	17,121	124,815
Slag, basic, ground or unground.....	13,186	130,455
All other substances used only for manure	154,729	3,314,460
<b>Total.....</b>	<b>955,436</b>	<b>10,819,253</b>

**MATERIAL ENTERING LARGELY INTO THE FERTILIZER INDUSTRY  
IN THE U. S. IN 1913**

Imports:	Quantity Long tons	Value Dollars
Potassium chloride.....	955,436	10,819,253
Potassium sulfate.....	212,170	7,075,745
Sodium nitrate.....	39,597	1,677,429
Domestic phosphate rock.....	612,861	21,630,811
	3,111,221	11,796,231
<b>Total.....</b>	<b>4,931,285</b>	<b>52,999,469</b>

**The Production of Manganese and Manganiferous Ores in 1913.** D. F. HEWETT. Separate No. 4 of Vol. 1. 20 pp. This report gives the various sources of manganese and the production summaries by districts, by mineral sources, and by years, and includes a discussion of the various manganese ores, the uses of manganese, and the importance of the various branches of the industry. In 1913 imports of manganese ore amounted to 345,000 long tons, having a value in excess of \$2,000,000. The American production formed only a very small fraction of the total world production, the three principal sources being Brazil, Russia and India. The uses of manganese in its various alloys and combinations are summarized under the following headings: (1) alloys; (2) oxidizers; (3) coloring materials; (4) flux in smelting silver and lead ores; (5) gems or ornamental stones, in the form of the minerals rhodonite and spessartite; (6) fertilizer; (7) various lesser chemical, manufacturing, and medical uses.

**Potash Salts.** W. C. PHALEN. Separate No. 7 of Vol. 2. 24 pp. Among the more important data given by this report are those referred to above under the heading of Phosphate Rock—the importance of the imported potash salts is evident from these tabulations.

**The Production of Talc and Soapstone in 1913.** J. S. DILLER. Separate No. 11, Vol. 2. 12 pp. Data of this report show that the United States is the largest producer of talc and soapstone and the American market will probably not be at all affected by any interruption of import facilities. It is to be noted that the production of California fell off markedly during 1913 but all other important producing states had material increases. The average per cent increase was 11.78 (for 1913 as compared with 1912).

**The Production of Silica.** FRANK J. KATZ. Separate No. 13, Vol. 2. 6 pp. The following tabulation gives a summary of the data included in this report:

**MARKETED PRODUCTION OF SILICA FOR POTTERY, PAINTS, FILLERS, POLISHERS, ABRASIVES, AND OTHER USES IN 1913, IN SHORT TONS**

	Quantity	Value Dollars
Quartz (vein quartz, (a) pegmatite and quartzite).....	97,902	201,488
Sand and sandstone (a).....	106,857	466,523
Tripoli.....	20,831	216,517
Diatomaceous earth.....	6,602	69,304
Flint.....	.....	.....
<b>Total.....</b>	<b>232,192</b>	<b>953,832</b>

(a) Includes only finely ground material.

**A New Gypsum Deposit in Iowa.** GEORGE F. KAY. Bulletin 580E. 6 pp. This is a separate from Part 1 of the 1913 "Contributions to Economic Geology."

**Oil Shale of Northwestern Colorado and Northeastern Utah.** E. J. WOODRUFF and DAVID T. DAY. Bulletin 581A. 20 pp. A separate from Part 2 of the 1913 "Contributions to Economic Geology."

**Oil and Gas in the Western Part of the Olympia Peninsula of Washington.** CHARLES F. LUPTON. Bulletin 581B. 60 pp. A separate from Part 2 of the 1913 "Contributions to Economic Geology."

**Coal Fields in Idaho, Washington and Oregon.** E. G. WOODRUFF and C. E. LESHNER. Bulletin 541I. 42 pp. An advance chapter from Part 2 of the 1912 "Contributions to Economic Geology."

**Celestite Deposits in California and Oregon.** W. C. PHALEN. Bulletin 540T. 12 pp. An advance chapter from Part 2 of the 1912 "Contributions to Economic Geology."

**Electrical Activity in Ore Deposits.** ROGER C. WELLS. Bulletin 548. 78 pp. This article reports on laboratory experimental work done with the object of investigating the electrical and electrolytic phenomenon which are of interest as having a bearing upon ore deposits. The general theoretical considerations are also fully discussed. In the preface it is emphasized "that the results thus far obtained afford no adequate basis for any method of electrical prospecting nor any promise of the development of such a method for making known the presence of ore deposits with readily or definitely measurable electrical activity."

**The Ore Deposits of Northeastern Washington.** HOWLAND BANCROFT. Including a Section of **The Republic Mining District** by WALDEMAR LINDGREN and HOWLAND BANCROFT. Bulletin 550. 215 pp. "Describes the geology of an area of about 6,000 square miles in Stevens and Ferry Counties, northeastern Washington, giving detailed information as to its mining districts and ore deposits—chiefly lead, zinc, and copper. States that the general conditions for mining are particularly favorable and discusses briefly the methods and costs of mining, treatment of the ores, and means of transportation. The illustrations include plans and sketch maps of some of the mines and halftone plates showing geologic conditions."

**Reconnaissance of Oil and Gas Fields in Wayne and McCreary Counties, Ky.** M. J. MUNN. Bulletin 579. 105 pp. "Gives a brief description of the stratigraphy and structure of the rocks in Wayne and McCreary Counties, Ky., with special reference to their oil and gas content. The oil and gas fields are treated in detail, and numerous records of wells are given. As to the future of the area, there is every reason to suppose that many other profitable oil pools will be found eventually in districts in and adjacent to Wayne County, and the structural conditions seem to favor the practical application of geology in finding these pools. The illustrations include sketch maps showing the location of oil and gas pools, sections of deep wells, and views of specimens from the Beaver Creek oil 'sand.'"

**BUREAU OF MINES**

**Selection of Explosives Used in Engineering and Mining Operations.** CLARENCE HALL and SPENCER P. HOWELL. Bulletin 48, 2nd Edition. 50 pp. Paper, 10 cents.

**Brass-Furnace Practice in the United States.** H. W. GILLET. Bulletin 73. 300 pp. Paper, 45 cts. "The object of the investigation reported in this bulletin was to ascertain the melting and fuel losses in present brass-melting practice and to indicate, as far as possible, methods by which these losses might be reduced." The magnitude of the losses is estimated to be about \$3,000,000 per year in metal alone. If the average metal loss could be reduced to be that found under best operating conditions there would be a saving of \$1,500,000 and if fuel efficiency and crucible life could be brought from present average to the best practice \$500,000 more could be saved.

Considerable difficulty was found in gathering technical information as a large number of companies are not operating with

technical control. Reports, however, indicate metal loss varying from 0.1 to 22 per cent and fuel efficiency from 1.5 to 16 per cent. In order to investigate the remedies for these conditions the relative advantages of different types of furnaces were studied as were the various operating practices affecting completeness of combustion, volatilization losses, and factors which produced irregularities in quality of metals. The causes of disease and danger and the essential precautions for the health and safety of workmen were also investigated and recommendations are given covering these subjects.

**Factors Governing the Combustion of Coal in Boiler Furnaces.** J. K. CLEMENT, J. C. W. FRAZER and C. E. AUGUSTINE. *Technologic Paper* 63. 45 pp. The object of the investigation reported in this paper was to determine the conditions requisite for an economic utilization of various types of coal. The more important factors influencing combustion which were investigated are: The volume and shape of the combustion chamber, the kind of fuel used, especially the amount and character of the volatile matter and rate of firing; the rate of heating the fuel; the air supply; the rate at which air is mixed with the combustible gases in the furnace; and the temperature of the combustion chamber. The preliminary report embodies the results of a series of 23 tests with Pocahontas coal. The furnace and its operation are described in detail, and the methods and apparatus used for gas analysis and making temperature measurements are given.

**Methods of Oil Recovery in California.** RALPH ARNOLD and V. R. GARFAS. *Technical Paper* 70. 57 pp. "In this paper are discussed the general methods employed in California for recovering the oil when, owing to insufficient gas pressure or other causes, it does not rise to the surface by natural flow. The report comprises a study of different pumping devices and means of generating power to operate them, and summarizes their relative cost and field of usefulness."

**Specific Gravity Separation Applied to the Analysis of Mining Explosives.** C. G. STORM and A. L. HYDE. *Technical Paper* 78. 13 pp. The article described various flotation methods for separating the constituents of explosives by differences in their specific gravity as a preliminary to the chemical analysis.

#### DEPARTMENT OF AGRICULTURE

**Progress Reports of Experiments in Dust Prevention and Road Preservation, 1913.** Bulletin 115. 46 pp. 5 cents. This contribution from the office of Public Roads gives the details of construction of several sample roads which have been constructed under the supervision of the Office of Public Roads. The various difficulties encountered and the results noted after the roads had been subject to traffic conditions for some time are reported in detail. Progress and supplementary reports are included for a number of roads for which specifications have previously been given.

#### HYGIENIC LABORATORY

**Gaseous Impurities in the Air of Railway Tunnels.** ATHON SEIDELL and PHILIP W. MESERVE. Bulletin No. 92. 47 pp. The investigation here reported was carried out in order to determine the amount of sulfur dioxide and carbon monoxide in the air of railway tunnels, and to point out what, if any, physiological difficulties might be expected from breathing such air. Methods for the determination of these impurities are discussed. Analyses of samples taken from the tunnels are given and the physiological effects of such impurities are discussed. It is probable that the concentration of these gases which was found was not sufficient to produce a serious effect upon man.

#### PUBLIC HEALTH SURVEY

**Soluble Aluminum Compounds; Their Occurrence in Certain Vegetable Products.** C. N. MYERS and CARL VOEGTLIN. *Public Health Reports*, 29, 1625-9 (No. 25, June 19, 1914). During an investigation into the causes of pellagra the relation of diet

to this disease was investigated and the possible relation of the considerable amounts of aluminum which is present in certain foods in large quantities in a water-soluble form was suggested as perhaps one of the causes of this disease. Data are given showing the quantity of aluminum present in various cereals and other vegetable foods from which it is concluded that "the daily consumption of aluminum on a mainly vegetable diet may assume large proportions."

**What is a Safe Drinking Water?** ALLEN J. McLOUGHLIN. *Public Health Reports*, 29, 1686-94 (No. 26, June 26, 1914). Data are given from 15 representative cities showing the efficiency of mechanical or rapid-sand filtration, slow-sand filtration, precipitation and disinfection, and disinfection alone in the purification of water. The number of *Bacillus coli* present in the purified water is used as a gauge of its quality. The importance of selecting raw water of as pure quality as possible is emphasized; and the need of a sufficient margin of safety for the operation of filter plants is pointed out.

#### WEATHER BUREAU

**Standard Units in Aerology.** *Monthly Weather Review*, 42, 141-43 (March, 1914). Several abstracts and articles are reviewed presenting the views and practice of some American physicists in the use of various units for pressure.

**Progress and Present State of Research on the Evaporation of Moisture in the Atmosphere.** A. WEILENMANN. *Monthly Weather Review*, 42, 158-64 (March, 1914). A mathematical development of the theories of evaporation together with a description of instruments and observations for the measurement of atmospheric evaporation are given as a review of the more important researches both theoretical and practical on this subject.

**Conversion of Barometric Reading into Standard Units of Pressure.** ROY M. COVERT. *Monthly Weather Review*, 42, 230-2 (April, 1914). Tables for converting barometric inches into millibars and barometric millimeters into millibars are given. These are based on the equivalent: Pressure in millibars equals 1.333305 times barometric height in millimeters.

#### CONSULAR REPORTS, JULY

The cost of crushing and pressing soya beans in Manchuria. (P. 24.)

Most of the salt manufactured in the Philippines is obtained by solar evaporation. (P. 17.)

Efforts are being made to increase the sale of American cotton seed cake and meal in Northern Europe. (P. 78.)

The production of gold in Siberia showed an increase in 1913. (P. 94.)

A new \$600,000 cement factory at Laguna, Philippines, is nearly completed. (P. 126.)

Among the products made from peat, in England, are peat charcoal (together with naphtha, ammonium sulfate, acetic acid, tar, and paraffin), manure, and paper (both brown and white). (P. 128.)

The manufacture of fertilizer from sponges and fish in the Bahamas is suggested. (P. 140.)

The increasing use of hardened (hydrogenated) oils is causing a decreased demand for copra (cocoanut oil) for use in the manufacture of soap, margarin, and compound lard. (P. 174.)

Natural soda deposits in British East Africa are being developed. (P. 182.)

The production of plantation rubber in Burma is increasing. (P. 217.)

The Widnes Corporation of England, which claims to furnish the cheapest gas in the world, has reduced the price of gas to \$0.24 per 1000 cu. ft. for general users and to \$0.16 per 1000 cu. ft. for motive power. (P. 233.)

Crude petroleum obtained in Japan is to be used extensively as fuel in the Japanese navy. (P. 236.)



The manufacture, importation, or sale of matches containing white phosphorus is prohibited in Canada after Jan 1, 1915. (P. 270.)

The bark of the black mangrove (*Avicennia nitida*) is recommended as a source of tanning extract. (P. 285.)

The nitrate industry in Chili is increasing. (P. 305.)

The cultivation of *esparto* and its preparation for the paper industry, in Almeria, Spain, is described. (P. 306.)

The zinc refining industry in Japan has increased so that Japan is now able to export zinc. (P. 308.)

The waste from sisal fiber is being used as a substitute for horse hair in cheap upholstery. (P. 313.)

The seed floss of the rubber vine (*Cryptostegia grandiflora*) cultivated in the Bahamas has been made into a light felt for use in life preservers. (P. 334.)

Experts from the Standard Oil Com. are drilling for oil in Northern China. (P. 353.)

The oils from the kukui nut of Hawaii and from the lumbang nut in the Philippines are similar to tung oil and useful for drying oils. (P. 376.) See THIS JOURNAL, 5, 644.

Additional platinum deposits have been discovered in Northern Ural, Russia. (P. 377.)

The cultivation and uses of kapols or "white silk cotton," obtained from the Siamese "nun" tree, are described. The fiber is mostly used for stuffing mattresses, etc. (P. 379-80.)

The specifications of steel railway ties used in Switzerland are given. (P. 379.)

A large oil refinery to handle Mexican crude oil is to be erected at Flushing, Holland. (P. 382.)

A new cement factory is to be erected in Siam. (P. 401.)

The sugar output of Cuba shows a decided increase. (P. 431.)

The production of plantation rubber in the Malay states shows an increase. (P. 479.)

Natural gas has been discovered in Temerin, Hungary. (P. 479.)

The methods and conditions of rubber cultivation in British Guiana are described. (P. 500.)

An apparatus for indicating electrically the presence and amount of methane in mine gas has been invented by an Englishman, and is known as Williams Fire Damp Indicator or Methanometer. No details are given. (P. 512.)

New uses for infusorial earth in this country and Europe include the manufacture of heat-insulating and fireproofing material, talking machine records, artificial fertilizers containing liquid manures, water glass, artificial stone, glazed tile, ultra-marine, paper, sealing wax, fireworks, gutta percha, safety matches, "solidified bromine," and papier-mâché. (P. 524.)

The use of dredges in mining tin ore on the Malay peninsula has resulted in an increased production of tin. (P. 525.)

The output of coal from Shantung, China, is increasing. (P. 552.)

The methods for the manufacture and liquefaction of sulfur dioxide in Austria are described. (P. 553.)

The cultivation of soya beans is replacing the poppy culture in China, since the suppression of the use of opium. (P. 553.)

Large amounts of copper sulfate are imported into Algeria for use as a germicide in the wine industry. (P. 554.)

The cottonseed products industry in India is described. (P. 556.)

The output of guano from Peru is increasing. (P. 559.)

The prospects for the sugar industry of Argentine and the Philippines are favorable. (P. 569.)

Experiments upon a cactus grown in Algeria, known as the "ficlu d' India" (*Opuntia*), have shown that the fruit contains 14 per cent of sugar, from which alcohol can be profitably produced. (P. 572.)

The prospects for the olive, cotton and sesame crops of Syria are promising. (P. 590.)

The hemp production of the United States is decreasing. (P. 598.)

Experiments in Sweden upon the use of powdered peat as fuel for railway engines have shown that 1.3 tons of Swedish peat is equivalent to 1.0 ton of English steam coal. (P. 622.)

Artificial silk and "horse hair" are now being made from cotton waste at Chemnitz, Germany. (P. 459.)

Statistics and information from consular agents regarding exports from various localities to the United States may be found as follows:

BELGIUM—p. 1-6	TURKEY—p. 110	COLOGNE—p. 427
Acids	Chrome ore	Alum dyes
Aluminum	Emery	Chemicals
Aniline dyes	Glue	Horn
Antimony	Gum mastic	Hides
Arsenic	Gum tragacanth	Mineral water
Asbestos	Licorice	Paints
Barytes	Olive oil	Drugs
Basic slag	Hides	HUNGARY—p. 491
Beeswax	Sesame	Aluminum
Bone meal	MANCHESTER, ENG.—p. 148	Casein
Chemicals	Asbestos	Glue
Clay	Chemicals	Antimony
Copper	Dyestuffs	Grease
Diamonds	Hides	Hides
Fertilizers	Linoleum	Magnesite
Fire brick	Paper stock	Mineral water
Glass	Steel wire	Oleostearin
Glue	Tin	Sugar
Glycerine	SICILY—pp. 296, 582	Wax
Gum copal	Asphalt	Wood pulp
Gum	Carbon bisulfide	AUSTRIA—p. 542
Hides	Citrate of lime	Aluminum
Lithopone	Hides	Chemicals
Naphthalene	Glue stock	Drugs
Nickel	Lemon juice	Enameled iron ware
Oils:	Licorice	Glass
Croosote	Essential oils	Hops
Lubricating	Olive oil	Magnesite
Sod	Paraffin	Meerschaaum
Vegetable	Sulfur	Ozokerite
Paraffine	Sumac extract	Wood pulp
Pebbles	Cream of tartar	Hides
Phosphates	NORTHERN FRANCE—pp. 347-9	Talc
Potash	Aniline dyes	Fats
Paper stock	Grease	Gelatin
Rubber	Lithopone	Bronze
Artificial silk	Nitrate	Ferrosilicou
Spelter	Sodium	Fusel oil
Stearin	Palm oil	Graphite
Tin	Paper stock	Paraffin
Wool grease	Potash	Artificial silk
Zinc oxide	Casein	Sugar beet seed
	Chalk	CANTON, CHINA—p. 551
	Glycerine	Antimony
	Fusel oil	Cassia
	EGYPT—p. 392	Raw silk
	Glue	TIENSIN, CHINA—p. 595
	Gum arabic	Beeswax
	Hides	Fire clay
	Fusel oil	Hides
	Paper stock	Glue
	Senna	Linsed
	Ivory	Apricot kernels
		Rape seed

## BOOK REVIEWS

**A Textbook of Thermodynamics.** (With special reference to Chemistry.) By JAMES RIDDICK PARTINGTON, M.Sc. (Vict.). New York: D. Van Nostrand Co. Cloth, 5 1/2 x 8 1/2 in. Pp. 544. 91 diagrams. Price, \$4.00 net.

The last decade has witnessed a marked change in the relationship between thermodynamics and engineering practice. Formerly, thermodynamics was regarded as an interesting study with but little practical use, and engineering work was carried on with the assistance of empiric formulae supplemented

by theories, which were in many cases formulated without true basis of fact and hence of doubtful value. To-day, however, the engineer is more and more discarding the empiric and seeking the rational. This change may be ascribed to two main reasons. One of these has been that the ever widening demands of industry have shown that in many cases the old empiric methods were applicable to only a narrow range of conditions and that a broader knowledge of fundamental cause and effect was essential. The other has been due to the fact that students

of thermodynamics, by a vast amount of study and experimental research, have made their subject of real value to practically every branch of industry.

Within the past few years a number of excellent works on thermodynamics have appeared, but most of these have paid particular attention to the problems related to power machinery and have given but scant attention to other phases of the subject. The author of the book, however, has seen the need of a clear presentation of that portion of thermodynamics which applies particularly to the requirements of students of physical chemistry and chemical engineers and he has endeavored to fulfill that need in this volume.

In support of the thermodynamic treatment of the subject matter the author says: "Thermodynamics deal with the various conditions under which heat energy is rendered available in physical and chemical systems. Energy changes are accompanied by definite changes in the variables defining the state of the system and the relation established between the quantities of energy leads to a relation between the properties of the system. No detailed knowledge of the exact way in which the energy changes occur in the system is required, and the methods of thermodynamics, as contrasted with those of the molecular theory, have the peculiarity that by their aid we can push forward the investigation of quantitative relations without waiting for more intimate knowledge of the structure of the system investigated. On the one hand this is a great gain, but on the other hand it is also a decided loss, since no information may be obtained about that structure by means of thermodynamics alone.

"For the purpose of interpretation, various hypotheses have been built up around the results which have been derived from the two laws of thermodynamics. It must not be forgotten, however, that the deductions of thermodynamics would stand quite firm if the whole hypothetical system collapsed about them."

The first portion of this volume is devoted to a clear exposition of the fundamental principles and the first two laws of thermodynamics which serve as a firm basis upon which to build the main subject matter of the book. This introductory portion is followed by a detailed consideration of fluids, ideal and permanent gases, changes of physical state, gas mixtures, dilute solutions, general theory of mixtures and solutions, capillarity and adsorption, electro-chemistry and kinetic theories in thermodynamics. The treatment of each subject considered consists of a brief but plain explanation of the theory involved coupled with a derivation of the mathematical relations between the governing factors. The sections devoted to mixtures and solutions are particularly valuable.

From one point of view it is to be regretted that the author has not included in the text more concrete examples which would serve to illustrate the application of the thermodynamic equations, but such omissions were doubtless made for the sake of brevity and possibly with the thought in mind that the instructor using this book as a text would be better able to judge the type of example best suited to any particular class of students. Used in connection with a lecture or laboratory course, this volume should prove a most valuable text, and while the author addresses it particularly to chemists there is much of the subject matter which should be taught to students of other branches of engineering.

HARRY L. PARR

**Industrial Organic Analysis.** For the Use of Technical and Analytical Chemists and Students. By PAUL S. ARUP, B.Sc., A.C.G.I., with a foreword by J. C. IRVINE, D.Sc., Ph.D. Published by P. Blakiston's Son & Co., Philadelphia. 340 pp. Price, \$2.00.

This little book is divided into eight chapters: Chapter I, Coal and Coke; Chapter II, Coal Tar and Its Distillation Products; Chapter III, The Fatty Oils and Fats; Chapter IV, Soap;

Chapter V, Petroleum and Its Distillation Products and Lubricating Oils; Chapter VI, Milk and Butter; Chapter VII, Starch and Its Decomposition Products, Flour, Barley and Malt; Chapter VIII, Preservatives and Artificial Coloring Matters in Foods.

In the preface the author says that he wrote this volume "for the use of students who, having received a thorough training in theoretical and practical chemistry, may desire to gain some insight into the methods and principles of industrial organic analysis, and as a work of reference for chemists engaged in technical or analytical work." He has succeeded in providing such an insight into methods of organic analysis as would be useful only for the man who follows industrial chemistry as a trade; it would hardly satisfy the advanced student or worker who is engaged in chemistry as a profession.

While the methods given are in general well described, the error of giving only one method in nearly all cases has been committed. There is no discussion of the merits of different methods of analyses, for example, in the chapter on the fatty oils nothing is said about the Hanus method for the determination of iodine absorption, the Hübl method is just mentioned and the Wijs method only is described. For the determination of reduced sugars by the Fehling method the modification of Brown, Morris and Millar is given with no mention of the other well known standard procedures. Such omissions, apart from the lack of variety of methods, render the book unsatisfactory as a text for American students.

The arrangement of the subject matter is rather peculiar. There are no chapters on Sugars or on Alcohols. One may, however, find a method for determining sucrose in the Soap chapter, a method for lactose in the subchapters on Condensed Milk, and a method for dextrose and maltose in the Starch chapter. There is no general description of the procedures to be used in the analysis of sugar mixtures. The specific gravity method for ethyl alcohol is described as a step in the process for determining starch by fermentation.

While there is a good list of reference books at the end of each chapter, the author repeatedly fails to supply journal references for most of the methods which he describes under the originators' names.

On account of the unique style this book can be recommended as a useful addition to the short works on organic analysis for those practising chemists who do not possess the more expensive reference treatises.

A. W. THOMAS

**Die Industrie der Cyanverbindungen, ihre Entwicklung und ihre gegenwärtiger Stand (The Industry of the Cyanogen Compounds, Its Development and Its Present Condition).** By HIPPOLYT KOEHLER. xiv + 200 pp. 30 ill. Crown 8vo. Friedrich Vieweg & Sohn, Brunswick, 1914. Price: Unbound, \$2.00; bound, \$2.25. Constituting part 8 of Engler's "Neues Handbuch der chemischen Technologie."

This book is divided into three main sections, viz.: I. Scientific Part, on the chemistry of cyanogen and cyanogen compounds. II. Technical Part, dealing with the manufacture from animal matter, atmospheric air, and from sulfo-cyanogen and ferrocyanogen compounds. Part III. Analytical Part, treating of the analysis of the cyanogen compounds, the raw materials, gas-works liquors, and the resulting products.

The introduction of six pages of historical interest contains copious references to the literature. A supplement of four pages of references to recent journal articles. The book closes with 11 pages of most excellent author and subject indexes.

The illustrations are good and well selected. Throughout the book there are a large number of references from the literature including patents. The typography is of the usual excellence which has come to be expected in all books published by Vieweg.

D. D. BEROLZHEIMER

**The Chemistry of Cattle Feeding and Dairying.** By J. ALAN MURRAY, B.Sc. (Edin.), Lecturer in Agricultural Chemistry at the University College, Reading. 8vo. 343 pp. 27 illustrations. Longmans, Green & Co. Price, \$1.75 net.

The scope of the present work is indicated by its four main subdivisions. Part I, Constituents of Plants and Animals, gives a brief presentation of the chemistry of carbohydrates, fats, and nitrogenous compounds. Part II, Requirements of Animals, treats of the fundamental problems of animal nutrition with reference to the various needs of maintenance, work, milk production, etc. Part III, Feeding Stuffs, discusses the composition of different fodders and feeding stuffs and the compounding of rations. Part IV, Dairying, considers the composition and chemistry of milk and milk products.

Probably no writer is more hampered by the restrictions of local or national usage than the author of a work upon cattle feeding. He is obliged by necessity to consider the needs of a limited public and his practical discussions, to be intelligible, must be governed by national custom. For this reason books upon cattle feeding suffer by translation; in order to reach a new public they must either be re-edited or re-written. The present work offers many illustrations of this. In discussing, for example, the economics of cattle feeding, the author must express all monetary values in pounds, shillings and pence, in order to be understood by his British readers. A very large number of cattle feeders are accustomed, however, to think in

dollars and cents, so that for this part of the English-speaking world the book loses greatly in practical value. In the same way when the author (p. 284) states that peat is the absorbent most commonly used in making molasses feeds and that such feeds should be valued solely for the amount of sugar they contain, he is evidently considering only local British conditions, for both statements are untrue as regards the molasses feeds sold in America.

Although the author professes to derive a part of his data from American experiments, his book gives one a very inadequate idea of the latest results of American research in the feeding of farm animals. A few pages might well have been devoted to the important investigations of Armsby and Fries at the Institute of Animal Nutrition of the Pennsylvania State College.

But notwithstanding that the work will have its chief value as a text-book and practical treatise for the British public, American students of cattle-feeding will find it a useful work of reference. The attempt of the author to break away from the tyranny of old rules is certainly to be commended and the novel presentation which he gives to several phases of his subject has many points of interest.

The typography and general make-up of the book are excellent. A good index is provided, but a bibliography is lacking.

C. A. BROWNE

## NEW PUBLICATIONS

By D. D. BEROLZHEIMER, Librarian The Chemists' Club, New York

**Agricultural Chemistry, A Manual of.** By HERBERT INGLE. Demy 8vo. 400 pp. Price, \$2.25. Scott, Greenwood & Co., London.

**Alcohol, Methyl, Analytical Chemistry of.** By HUGO BAUER. 8vo. 73 pp. Price, \$0.75. Ferdinand Enke, Stuttgart. (German.)

**Anesthesia.** By JAMES W. GATHWAY in collaboration with CHAS. BASKERVILLE. Price, \$6.00. D. Appleton & Co., New York

**Chemical Industry, Yearbook of the Austrian, 1913.** 8vo. Price, \$1.00. Kompassverlag, Vienna. (German.)

**Drug Assay Methods, Biochemic.** By PAUL S. PITTENGER AND F. E. STEWART. 8vo. 158 pp. Price, \$1.50. P. Blakiston's Son & Co., Philadelphia.

**Explosives.** By H. BRUNSWIG. 2d Ed. 8vo. 158 pp. Price, \$0.25. G. J. Goeschen, Berlin. (German.)

**Explosives, Lectures on.** By WILLIAM McNAB. 8vo. 67 pp. Price, \$0.75. Institute of Chemistry, London.

**Fermentation, Alcoholic.** By ARTHUR HARDEN. 8vo. 150 pp. Price, \$1.00. Longmans, Green & Co., New York.

**Filtration, Technic of.** By HEINRICH METZGER. 8vo. Price, \$1.25. A. Hartleben, Vienna. (German.)

**Food Materials, Human, The Chemistry of.** Vol. III, Part 2. The Animal and Vegetable Food Materials. By J. KOENIG. Vol. 3, 4th Ed. L. 8vo. 972 pp. Price, \$9.00. Julius Springer, Berlin.

**Fuel, Examination of Thermal Value of Gaseous, Liquid and Solid.** By J. H. COSTE AND E. R. ANDREWS. 8vo. 278 pp. Price, \$1.50. Charles Griffin & Co., London.

**History of Chemistry.** By E. von MEYER. 4th Ed. L. 8vo. 616 pp. Price, \$3.50. Veit & Co., Leipzig. (German.)

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**Indicator, The, and Its Utilization.** By P. H. ROSENKRANZ. 7th Ed. L. 8vo. 522 pp. Price, \$4.00. Weidmannsche Buchhandlung, Berlin. (German.)

**Iron, History of Electro-, with Special Reference to the Electric Furnaces for Its Production.** By OSTWALD MEYER. 8vo. 200 pp. Price, \$2.00. Julius Springer, Berlin. (German.)

**Metalurgy, Principles of.** By ARTHUR H. HIGGINS. 2d Ed. 8vo. 389 pp. Price, \$1.50. Macmillan Co., New York.

**Mineralogy, The Fundamentals of Chemistry and.** By R. ARENDT. 11th Ed. L. 8vo. 517 pp. Price, \$1.25. Leopold Voss, Leipzig. (German.)

**Nitrogen, Atmospheric, The Industry of.** By ALFRED TOBIANSKY D'ALTOFF. 8vo. Dunod & Pinat, Paris. (French.)

**Organic Compounds, Detection of.** By L. ROSENTHALER. L. 8vo. 1070 pp. Price, \$8.00. Ferdinand Enke, Stuttgart. (German.)

**Organic Section (Condensed) of Text-Book of Chemistry.** By A. PARTHELL AND R. OTTO. 8vo. Price, \$4.50. Carl Georgi, Bonn. (German.)

**Textil Soap and Oils.** By G. H. HURST. 2d Ed. 8vo. 202 pp. Price, \$2.00. Scott, Greenwood & Co., London.

**Titrations, The Theory of Alkalimetric and Acidimetric.** By N. BJERRUM. L. 8vo. 128 pp. Price, \$1.20. Ferdinand Enke, Stuttgart. (German.)

**Vanadium, Chemical Technology of.** By G. FESTER. 8vo. 79 pp. Price, \$0.75. F. Enke, Stuttgart. (German.)

**Vegetable Kingdom, The Raw Materials of the.** By J. von WEISNER. 3d Ed. L. 8vo. 579 pp. Price, \$7.00. Wilhelm Engelmann, Leipzig. (German.)

### RECENT JOURNAL ARTICLES

**Alloys, Iron-Magnesium, Experiments on the Electrolytic Separation of, from Aqueous Solutions.** By R. KREIMANN AND J. LORBER. *Monatshefte fuer Chemie*, Vol. 35, 1914, No. 6, pp. 603-634.

**Analysis, Metal, Progress in, in 1913.** By TH. DOERING. *Chemiker Zeitung*, Vol. 38, 1914, No. 84, pp. 893-894.

**Asphalt, Navajo.** By TH. ROSENTHAL. *Zeitschrift fuer angewandte Chemie*, Vol. 27/1, 1914, No. 54, pp. 422-424.

**Asphalts, Contributions to the Chemistry and Analysis of.** By J. MARCUSSON. *Chemiker Zeitung*, Vol. 38, 1914, No. 76 and 77, pp. 813-815, 822-823.

**Catalysis.** By P. SABATIER. *Chemical Trade Journal*, Vol. 55, 1914, No. 1416, pp. 23-24.

**Cement, Portland; Philippine Raw Materials.** By AUGUSTUS P. WEST AND ALVIN J. COX. *Philippine Journal of Science*, Vol. A 9, 1914, No. 1, pp. 79-103.

**Copper, Precipitation of, from Solution at Anaconda.** By FREDERICK LAIST AND F. F. FRICK. *Bulletin of the American Institute of Mining Engineers*, 1914, No. 91, pp. 1425-1446.

**Efficiency, The Taylor System of, Its Economic Significance and Its Utilization in Chemical Industry.** By WILHELM KOCHMANN. *Zeitschrift fuer angewandte Chemie*, Vol. 27/1, 1914, No. 56, pp. 425-436.

**Electrolytic Dissociation, The Theory of.** By SVANTE ARRHENIUS. *Journal of the Chemical Society*, Vol. 105, 1914, No. 629, pp. 1414-1426.

**Fats, Determination of Resins in.** By HANS WOLFF. *Seifenfabrikant*, Vol. 34, 1914, No. 27, pp. 745-747.

**Fermentation Industry, Progress in the, in 1913.** By O. MOHR. *Zeitschrift fuer angewandte Chemie*, Vol. 27/1, 1914, No. 50, pp. 361-368.

**Fertilizers, Radioactive.** By JULIUS STOKES. *Chemiker Zeitung*, Vol. 38, 1914, No. 79, pp. 841-844.

**Foundry Sands and Their Treatment.** By ALGERNON I. CURTIS. *Metal Industry*, Vol. 12, 1914, No. 6, pp. 241-243.



- Fuel: Illuminating Gas, Coke and Generator Gas in 1913.** By ARTHUR FULFERT. *Zeitschrift fuer angewandte Chemie*, Vol. 27, 1, 1914, No. 52, pp. 385-407.
- Fuels, the Solid, in the Years 1912 and 1913.** By W. BERTELSMANN. *Chemiker Zeitung*, Vol. 38, 1914, Nos. 75 and 80, pp. 797-798 and 853-855.
- Gas Analysis by Fractional Distillation at Low Temperatures.** By G. A. BURRILL AND F. M. SEIBERT. *Chemical News*, Vol. 110, 1914, Nos. 2849 and 2850, pp. 2, 5 and 14-19.
- Glasses: Tellurium as Coloring Matter for Soda-Lime-Silicates.** By PIERO FENAROLI. *Chemiker Zeitung*, Vol. 38, 1914, No. 82, pp. 873-874.
- Glover and Gay-Lussac Towers, Apparatus for.** By WILLIAM MASON. *Chemiker Zeitung*, Vol. 38, 1914, No. 75, pp. 800-801.
- Guncotton, Determination of Nitrogen in, by Means of the Nitrometer.** By E. G. BECKETT. *Journal of the Society of Chemical Industry*, Vol. 33, 1914, No. 12, pp. 628-631.
- Leather, Rehbein Method of Determining Sulfuric Acid in.** By W. J. KELLEY. *Journal of the American Leather Chemists' Association*, Vol. 9, 1914, No. 8, pp. 340-354.
- Metals, The Hardening of.** By C. A. EDWARDS AND H. C. H. CARPENTER. *Engineering*, Vol. 97, 1914, No. 2530, pp. 885-891.
- Mineral Oil Mixtures, Simple Method for the Calculation of the Degree of Viscosity of.** By EINAR MOLIN. *Chemiker Zeitung*, Vol. 38, 1914, No. 81, pp. 857-859.
- Oil, Chinese Wood, Examination of.** By E. E. WARE AND C. L. SCHUMANN. *Drugs, Oils and Paints*, Vol. 30, 1914, No. 2, pp. 52-54.
- Paint: Researches on Drying Oils.** By J. NEWTON FRIEND. *Drugs, Oils and Paints*, Vol. 30, 1914, No. 2, pp. 50-52.
- Paints, The Drying of.** By J. CRUCKSHANK SMITH. *Paint, Oil and Drug Review*, Vol. 58, 1914, No. 3, pp. 10, 12-13.
- Paper Testing, Systematic.** By J. F. BRIGGS. *Paper*, Vol. 14, 1914, No. 17, pp. 15-17 and 38.
- Patents and Inventions.** By HAROLD E. POTTS. *India Rubber Journal*, Vol. 47, 1914, No. 23, pp. 1127-1128, 1131-1132 and 1134.
- Petroleum, Chemistry and Technology of, in the Year 1913.** By L. GURWITSCH. *Zeitschrift fuer angewandte Chemie*, Vol. 27/1, 1914, No. 58, pp. 441-447.
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- Radio-elements, Distribution of, in Rocks. I. On Monazite Sand.** By M. BALUCH AND G. MEISSNERBERGER. *Zeitschrift anorganische Chemie*, Vol. 88, 1914, No. 1, pp. 88-102.
- Radium Emanation, Quantitative Determination of the, in the Atmosphere, and Its Variation with Altitude and Meteorological Conditions.** By J. R. WRIGHT AND O. F. SMITH. *Philippine Journal of Science*, Vol. A, 9, 1914, No. 1, pp. 51-77.
- Refractory Materials.** By GILBERT RIGG. *Journal of the Society of Chemical Industry*, Vol. 33, 1914, No. 12, pp. 619-626.
- Research Work in the Laboratory and Mill.** By WARREN F. BLEEKER. *Metallurgical and Chemical Engineering*, Vol. 12, 1914, No. 8, pp. 515-523.
- Steam Distribution, Increased Efficiency in.** By JOHN W. BRASSINGTON. *Paper*, Vol. 14, 1914, No. 18, pp. 15-17.
- Steel, Carbon, Heat Treatment of.** By HUGH P. TIEMANN. *Chemical Engineer*, Vol. 20, 1914, No. 1, pp. 18-25.
- Steels, Carbon, Relations between the Solidity and the Structural and Chemical Composition of.** By W. MUELLER. *Dingler's Polytechnisches Journal*, Vol. 329, 1914, No. 28, pp. 437-440.
- Sugars, the Valuation of Raw.** By F. G. WIECHMANN. *Sugar*, Vol. 16, 1914, No. 8, pp. 27-31.
- Sulfur Production from Ores in Europe.** O. URBASCH. *Chemiker Zeitung*, Vol. 38, 1914, No. 83, p. 899.
- Sulfuric Acid, The Detection of Very Small Amounts of Selenic Acid in.** By ERNST SCHMIDT. *Archiv der Pharmazie*, Vol. 252, 1914, No. 3, pp. 161-165.
- Textile Manufacturing, Oils and Soaps Used in.** By HERBERT CARTER. *Canadian Textile Journal*, Vol. 31, 1914, No. 7, pp. 191-193.
- Tungsten, Studies on the Analytical Examination of.** By HANS ARNOLD. *Zeitschrift fuer anorganische Chemie*, Vol. 88, 1914, No. 1, pp. 74-87.
- Water Analysis: Two Reliable Methods for the Colorimetric Determination of Lead and Copper in Drinking Water.** By C. REESE AND J. DROST. *Zeitschrift fuer angewandte Chemie*, Vol. 27/1, 1914, No. 42, pp. 307-312.
- Water, Feed-, Treatment.** By EDWARD H. ROBIE. *Practical Engineer*, Vol. 18, 1914, No. 12, pp. 633-634.
- Water Purification by Means of Magnesia.** By BOHLIG AND ROTH. *Chemiker Zeitung*, Vol. 38, 1914, No. 81, pp. 859-860.
- Zinc, Losses of, in Mining, Milling and Smelting.** By DORSEY A. LYON AND SAMUEL S. ARENTZ. *Bulletin of the American Institute of Mining Engineers*, 1914, No. 91, pp. 1411-1423.
- Zinc, Metallic Liquid, Continuous Production of, in the Shaft Furnace.** By A. RZCHULEA. *Chemiker Zeitung*, Vol. 38, 1914, No. 84, pp. 895-897.

## RECENT INVENTIONS

By C. L. PARKER, Solicitor of Chemical Patents, McGill Building, Washington, D. C.

**Waterproof Concrete.** R. K. Meade, April 14, 1914. U. S. Pat. 1,092,933. A powdered filler, the particles of which are coated with a very thin film of mineral oil, is mixed with the concrete to render it waterproof.

**Purifying Aluminum and Its Alloys.** G. Mellen, April 14, 1914. U. S. Pat. 1,092,936. The aluminum or alloy is melted and sulfur vapors are bubbled through it.

**Rubber from Hydrocarbons.** R. B. Earle, April 21, 1914. U. S. Pat. 1,093,923. Isoprene is saturated with dry ammonia gas and subjected to heat and pressure.

**Varnish Composition for Cement Floors.** S. Cabot, April 21, 1914. U. S. Pat. 1,094,118. This is a flexible coating composition comprising a mixture of wood fiber varnish, and zinc oxide, the fiber being arranged to permit the passage of moisture by capillary action.

**Production of Ammonia.** Bosch, Mittasch and Wolf, April 21, 1914. U. S. Pat. 1,094,194. A mixture of nitrogen and hydrogen free from contact poison is passed over an active catalyst containing cobalt and alumina.

**Printing Ink.** M. Wolff, April 21, 1914. U. S. Pat. 1,094,288. The ink contains peat, an alkaline silicate, a pigment, oily matter derived from petroleum and resin oil.

**Purifying Water from Germs by Means of Bromin.** M. Riegel, April 28, 1914. U. S. Pat. 1,094,475. To the water is simultaneously added hydrochloric acid and a solution of bromin in potassium bromid. The free acid and the free bromin are

then removed from the water by adding a predetermined quantity of a mixture of sodium sulfate and sodium carbonate.

**Removing Tin from Phosphate Liquors Used in Weighting Silk.** E. Meili, April 28, 1914. U. S. Pat. 1,094,671. This is a process for the regeneration of used phosphate baths employed in the weighting of silk and consists in precipitating the tin and other metallic impurities in the bath by means of silicic acid.

**Fume-Destroying Process.** S. W. Young, April 28, 1914. U. S. Pat. 1,094,767. Sulfurous fumes are treated to remove the sulfur dioxide and to produce free sulfur. The fumes are passed through a heated space, mixed with highly heated carbonaceous material in the presence of lime and cooled to a temperature at which the sulfur formed will not combine with oxygen.

**Non-Inflammable Varnish Composition.** J. W. Aylsworth, April 28, 1914. U. S. Pat. 1,094,830. The composition comprises approximately equal parts of a phenol resin and acetyl cellulose dissolved in ten times its weight of acetylene tetrachlorid.

**Producing Available Phosphoric Acid.** W. S. Landis, April 28, 1914. U. S. Pat. 1,094,857. Finely divided phosphate rock is mixed with sodium sulfate and the mixture treated with water. The mixture is then dried so quickly as to prevent the sodium sulfate from crystallizing to an appreciable extent, and the dried mixture is then calcined.

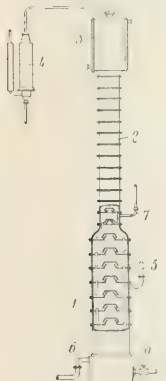
**Varied Colorations and Black Shades on Metals.** F. A. Roux, May 5, 1914. U. S. Pat. 1,095,357. The metal to be

treated is immersed in an electrolytic bath compound of ammonium molybdate and a current is passed between the metal as a cathode and an inert anode.

**Isoprene.** A. Heinemann, May 20, 1914. U. S. Pat. 1,095,395. Isoprene is produced by passing the vapors of turpentine oil over heated copper.

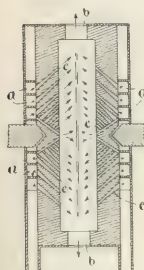
**Purifying Alcohol Manufactured by Distilling Fermented Sulfite Liquor.** G. Ekström, May 5, 1914. U. S. Pat. 1,095,830. Fermented sulfite liquor contains besides alcohol small quantities of more or less volatile compounds, such as sulfurous acid, aldehydes and ketones which follow the alcohol during the distillation process and make the final product impure and which also partly affect the material of the distilling apparatus.

The process consists in treating the alcohol with bases during the distillation of the sulfite liquor itself, while the alcohol and the impurities accompanying the same are in form of steam or vapor. The base, for instance, carbonate of sodium, is introduced directly into the distilling apparatus, or one may provide a separate purifying apparatus charged with the basic purifying agent, through which the weak alcohol vapor distilled from the sulfite liquor is led, before it is led through the other parts of the apparatus to be concentrated and condensed.



In the use of the apparatus illustrated the liquor to be distilled is admitted continuously through the pipe 5 and flows successively downward through the apparatus and escapes through the pipe 6. On its way through the apparatus 1, the liquor meets steam supplied through the pipe 9, by which the alcohol together with some impurities, such as sulfurous acid, and aldehyde compounds are driven off as vapor. These vapors pass upward through the column. During the passage of these vapors through that portion of the column which is charged with a basic agent and which is situated between the supply pipe 7 and the liquor supply pipe 5, the sulfurous acid accompanying the alcohol vapors is bound by the basic agent, while other vapors, such as aldehyde-sulfurous-acid or acetaldehyde-sulfurous-acid, are decomposed so that the free aldehyde and sulfurous acid are formed. The aldehyde accompanies the alcohol vapors and may be separated from the gases remaining after the condensation of the concentrated alcohol, while the sulfurous acid will be bound to the sodium.

When the alcohol vapors in this manner have been freed from injurious impurities the concentration and condensation are accomplished in the usual manner in the other parts of the plant.



**Electric Furnace.** A. Scott Hansen, May 12, 1914. U. S. Pat. 1,096,321. This is a furnace with magnetically spread disk shaped flames having passages for blowing currents of air or gas from the sides of the furnace toward the flame disk into the furnace chamber, the passages being so directed that the currents, considered as a whole, will assume the form of truncated cones having a common base in the plane of the flame disk.

**Antimony Oxid.** A. L. Stark, May 12, 1914. U. S. Pat. 1,096,468. Powdered antimony sulfid is ignited while in a state of suspension, thereby producing a mixture of antimony oxid

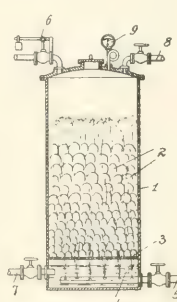
and sulfur dioxide. Such oxides are cooled immediately after they are formed, so as to prevent the formation of antimonious oxid and the antimony oxid is then separated from the other products of combustion.

**Acetaldehyde.** Erich Baum and Martin Mugdan, May 12, 1914. U. S. Pat. 1,096,667. Acetaldehyde is produced by causing acetylene to react with a solution of sulfuric acid containing mercury sulfate as catalyst at a temperature at which the acetaldehyde distills from the solution and at a concentration of acid of not higher than 6 per cent.

**Gas Process and Product.** W. O. Snelling, May 12, 1914. U. S. Pat. 1,096,797. Acetylene is dissolved under pressure in a liquefied natural gas comprising one or more paraffin hydrocarbons held under pressure in liquid form, whereby the solvent escapes with the acetylene and is combustible therewith.

**White Lead.** A. S. Ramage, May 26, 1914. U. S. Pat. 1,097,672. Basic carbonate of lead is prepared from lead sulfate by reacting upon it with an alkali carbonate in less proportion than is required for the conversion of all of the sulfate into carbonate. The product is then treated with an alkali hydroxide.

**Lead Salts of Acetic Acid.** F. J. Kalkow, May 19, 1914. U. S. Pat. 1,097,099. In this process lead salts of acetic acid are manufactured from lead using air as an oxidant and either acetic acid or an aqueous solution of normal lead acetate as solvent.



In the practice of the process a mass of lead, 2, is supported on a grate, 3. The solvent 4 is on the bottom of the vessel and the surface of the liquid is just below the grating 3, although the level of the liquid may vary within certain limits. Through pipe 5 air under pressure is admitted into the liquid and in rising carries liquid with it into the mass of lead which it sprinkles as it flows back to the bottom of the vessel. The compressed air leaves the vessel through a pipe provided with a safety valve, 6. The liquid may be withdrawn through the pipe 7. It is preferable to empty the vessel of liquid by admitting compressed air through a pipe, 8.

**Hydrogenated Oil.** C. Ellis, May 19, 1914. U. S. Pat. 1,097,308. This composition consists of catalytically-hardened edible cottonseed oil of lard-like consistency, free from dissolved metal catalyst.

**Sugar.** A. L. Mathews, May 26, 1914. U. S. Pat. 1,097,724. Sugar juices containing relatively large amounts of glucose are purified by making them alkaline with lime while maintaining them at a temperature not above 50° C. The solution is then brought to a neutral condition and heated to a higher temperature to remove impurities precipitated by heat.

**Cleaning Metal Surfaces.** C. H. Thompson, May 26, 1914. U. S. Pat. 1,098,338. This process involves the employment of a bath of any suitable chlorid, sulfate or nitrate solution, passing an alternating current through this bath, separating the electrodes from the articles to be treated by perforated or porous partitions, and placing the articles in the bath without any metallic connection with the electrodes.

# MARKET REPORT

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR THE MONTH OF AUGUST, 1914

## ORGANIC CHEMICALS

Acetanilid.....	Lb.	—	@	—
Acetic Acid (28 per cent).....	C.	1.50	@	1.65
Acetone (drums).....	Lb.	10 <sup>1</sup> / <sub>2</sub>	@	11
Alcohol, denatured (180 proof).....	Gal.	33	@	35
Alcohol, grain (188 proof).....	Gal.	2.50	@	2.52
Alcohol, wood (95 per cent).....	Gal.	45	@	47
Amyl Acetate.....	Gal.	2.25	@	2.30
Aniline Oil.....	Lb.	—	@	—
Benzoic Acid.....	Lb.	—	@	—
Benzol (90 per cent).....	Gal.	—	@	—
Camphor (refined in bulk).....	Lb.	51	@	55
Carbolic Acid (drums).....	Lb.	38	@	40
Carbon Bisulfide.....	Lb.	8	@	10
Carbon Tetrachloride (drums).....	Lb.	—	@	15
Chloroform.....	Lb.	25	@	30
Citric Acid (domestic), crystals.....	Lb.	75	@	80
Dextrine (corn).....	C.	3.07	@	3.32
Dextrine (imported potato).....	Lb.	—	@	—
Ether (U. S. P., 1900).....	Lb.	18	@	24
Formaldehyde.....	Lb.	8 <sup>1</sup> / <sub>2</sub>	@	9 <sup>1</sup> / <sub>2</sub>
Glycerine (dynamite), domestic.....	Lb.	21	@	25
Oxalic Acid.....	Lb.	23	@	25
Pyrogallous Acid (bulk).....	Lb.	—	@	—
Salicylic Acid.....	Lb.	50	@	75
Starch (cassava).....	Lb.	3 <sup>1</sup> / <sub>4</sub>	@	4
Starch (corn).....	C.	2 29	@	2.40
Starch (potato).....	Lb.	—	@	—
Starch (rice).....	Lb.	—	@	—
Starch (sago).....	Lb.	—	@	—
Starch (wheat).....	Lb.	5	@	10
Tannic Acid (commercial).....	Lb.	55	@	60
Tartaric Acid, crystals.....	Lb.	38	@	40

## INORGANIC CHEMICALS

Acetate of Lead (brown, broken).....	Lb.	7 <sup>1</sup> / <sub>4</sub>	@	7 <sup>1</sup> / <sub>2</sub>
Acetate of Lime (gray).....	C.	1.50	@	1.55
Alum (lump).....	C.	1.75	@	2.00
Aluminum Sulfate (high-grade).....	C.	1.25	@	1.75
Ammonium Carbonate, domestic.....	Lb.	10	@	11
Ammonium Chloride, gray.....	Lb.	6 <sup>1</sup> / <sub>2</sub>	@	7
Aqua Ammonia (drums) 16°.....	Lb.	2 <sup>1</sup> / <sub>4</sub>	@	2 <sup>1</sup> / <sub>2</sub>
Arsenic, white.....	Lb.	4 <sup>1</sup> / <sub>2</sub>	@	5
Barium Chloride.....	Lb.	—	@	—
Barium Nitrate.....	Lb.	—	@	—
Barytes (prime white, foreign).....	Ton	—	@	—
Bleaching Powder (35 per cent).....	C.	3.00	@	3.50
Blue Vitriol.....	C.	4.50	@	4.75
Borax, crystals (bags).....	Lb.	3 <sup>3</sup> / <sub>4</sub>	@	4 <sup>1</sup> / <sub>2</sub>
Boric Acid, crystals (powd.).....	Lb.	7 <sup>3</sup> / <sub>4</sub>	@	8
Brimstone (crude, domestic).....	Ton	22.00	@	22.50
Bromine, bulk.....	Lb.	40	@	50
Calcium Chloride, fused.....	C.	60	@	65
Chalk (light precipitated).....	Lb.	8	@	10
China Clay (imported).....	Ton	—	@	—
Feldspar.....	Ton	—	@	—
Fuller's Earth, powdered, Foreign.....	Ton	—	@	—
Green Vitriol (bulk).....	C.	55	@	60
Hydrochloric Acid (18°).....	C.	1.15	@	1.65
Iodine (resublimed).....	Lb.	3.75	@	4 00
Lead Nitrate.....	Lb.	8 <sup>1</sup> / <sub>2</sub>	@	9
Litharge (American).....	Lb.	5 <sup>1</sup> / <sub>4</sub>	@	5 <sup>1</sup> / <sub>2</sub>
Lithium Carbonate.....	Lb.	65	@	70
Magnesium Carbonate.....	Lb.	—	@	—
Magnesite "Calcined".....	Ton	55.00	@	—
Nitric Acid, 36°.....	Lb.	3 <sup>7</sup> / <sub>4</sub>	@	4 <sup>1</sup> / <sub>4</sub>
Phosphoric Acid (sp. gr. 1.75).....	Lb.	20	@	24
Phosphorus.....	Lb.	—	@	—
Plaster of Paris.....	Bbl.	1.50	@	1.70
Potassium Bichromate, 50°.....	Lb.	9	@	10
Potassium Bromide.....	Lb.	55	@	60
Potassium Carbonate (calcined), 80 @ 85%.....	C.	—	@	15
Potassium Chlorate, crystals.....	Lb.	—	@	—
Potassium Cyanide (bulk), 98-99%.....	Lb.	25	@	30
Potassium Hydroxide.....	C.	22.00	@	—
Potassium Iodide (bulk).....	Lb.	2.95	@	3.00
Potassium Nitrate (crude).....	Lb.	8	@	—
Potassium Permanganate (bulk).....	Lb.	—	@	50
Quicksilver, Flask (75 lbs.).....	90.00	@	100.00	@
Red Lead (American).....	Lb.	6	@	6 <sup>1</sup> / <sub>4</sub>
Salt Cake (glass makers').....	C.	55	@	65

Silver Nitrate.....	Oz.	37	@	38
Soapstone in bags.....	Ton	10.00	@	12.00
Soda Ash (48 per cent).....	C.	67 <sup>1</sup> / <sub>2</sub>	@	72 <sup>1</sup> / <sub>2</sub>
Sodium Acetate.....	Lb.	3 <sup>3</sup> / <sub>4</sub>	@	4 <sup>1</sup> / <sub>8</sub>
Sodium Bicarbonate (domestic).....	C.	1.00	@	1.10
Sodium Bicarbonate (English).....	Lb.	—	@	—
Sodium Bichromate.....	Lb.	4 <sup>1</sup> / <sub>4</sub>	@	5
Sodium Carbonate (dry).....	C.	60	@	80
Sodium Chlorate.....	Lb.	7 <sup>1</sup> / <sub>4</sub>	@	7 <sup>1</sup> / <sub>2</sub>
Sodium Hydroxide, 60 per cent.....	C.	1.55	@	1.57 <sup>1</sup> / <sub>2</sub>
Sodium Hyposulfite.....	C.	1.30	@	1.60
Sodium Nitrate, 95 per cent, spot.....	C.	2.20	@	—
Sodium Silicate (liquid).....	C.	65	@	1.50
Strontium Nitrate.....	Lb.	—	@	—
Sulfur, Flowers (sublimed).....	C.	2.20	@	2.60
Sulfur, Roll.....	C.	1.85	@	2.15
Sulfuric Acid, 60° B.....	C.	85	@	1.00
Talc (American).....	Ton	15.00	@	20.00
Terra Alba (American), No. 1.....	C.	75	@	80
Tin Bichloride (50°).....	Lb.	15	@	25
Tin Oxide.....	Lb.	65	@	70
White Lead (American, dry).....	Lb.	5 <sup>1</sup> / <sub>4</sub>	@	5 <sup>1</sup> / <sub>2</sub>
Zinc Carbonate.....	Lb.	8 <sup>1</sup> / <sub>2</sub>	@	9
Zinc Chloride (granulated).....	Lb.	4 <sup>1</sup> / <sub>2</sub>	@	5
Zinc Oxide (American process).....	Lb.	5 <sup>1</sup> / <sub>8</sub>	@	6 <sup>1</sup> / <sub>8</sub>
Zinc Sulfate.....	C.	2.35	@	2.70

## OILS, WAXES, ETC.

Beeswax (pure white).....	Lb.	47 <sup>1</sup> / <sub>2</sub>	@	50
Black Mineral Oil, 29 gravity.....	Gal.	13 <sup>1</sup> / <sub>2</sub>	@	14
Castor Oil (No. 3).....	Lb.	—	@	—
Ceresin (yellow).....	Lb.	12	@	22
Corn Oil.....	C.	6.35	@	6.40
Cottonseed Oil (crude), f. o. b. mill.....	Gal.	38	@	40
Cottonseed Oil (p. s. y.).....	Lb.	6 <sup>1</sup> / <sub>4</sub>	@	7
Cylinder Oil (light, filtered).....	Gal.	21 <sup>1</sup> / <sub>2</sub>	@	32
Japan Wax.....	Lb.	—	@	13
Lard Oil (prime winter).....	Gal.	92	@	95
Linseed Oil (raw).....	Gal.	58	@	60
Menhaden Oil (crude).....	Gal.	35	@	—
Neatsfoot Oil (20°).....	Gal.	96	@	98
Paraffine (crude, 120 & 122 m. p.).....	Lb.	3 <sup>1</sup> / <sub>8</sub>	@	3 <sup>1</sup> / <sub>4</sub>
Paraffine Oil (high viscosity).....	Gal.	27	@	28
Rosin ("E" grade) (280 lbs.).....	Bbl.	4.10	@	—
Rosin Oil (first run).....	Gal.	—	@	27
Shellac, T. N.....	Lb.	21	@	22
Spermaceti (cake).....	Lb.	30	@	31
Sperm Oil (bleached winter), 38°.....	Gal.	70	@	71
Spindle Oil, No. 200.....	Gal.	18	@	19
Stearic Acid (double-pressed).....	Lb.	8 <sup>3</sup> / <sub>4</sub>	@	9
Tallow (acidless).....	Gal.	64	@	66
Tar Oil (distilled).....	Gal.	30	@	31
Turpentine (spirits of).....	Gal.	44	@	45

## METALS

Aluminum (No. 1 ingots).....	Lb.	20	@	20 <sup>1</sup> / <sub>2</sub>
Antimony (Hallet's).....	Lb.	16	@	18
Bismuth (New York).....	Lb.	2.10	@	2.15
Bronze powder.....	Lb.	—	@	—
Copper (electrolytic).....	Lb.	12.12 <sup>1</sup> / <sub>2</sub>	@	—
Copper (lake).....	C.	12.37 <sup>1</sup> / <sub>2</sub>	@	—
Lead, N. Y.....	C.	3.85	@	—
Nickel.....	Lb.	50	@	55
Platinum (refined).....	Oz.	—	@	—
Silver.....	Oz.	—	@	—
Tin.....	C.	49.00	@	50.00
Zinc.....	C.	6.00	@	6.10

## FERTILIZER MATERIALS

Ammonium Sulfate.....	C.	3.25	@	—
Blood, dried.....	Unit	3.35	@	—
Bone, 4 <sup>1</sup> / <sub>2</sub> and 50, ground, raw.....	Ton	27.50	@	—
Calcium Cyanamid.....	Unit of Ammonia	2.17 <sup>1</sup> / <sub>2</sub>	@	2.20
Calcium Nitrate (Norwegian).....	C.	—	@	—
Castor meal.....	Unit	—	@	—
Fish Scrap, domestic, dried.....	Unit	3.40	@	10
Phosphate, acid, 16 per cent bulk.....	Ton	7.50	@	—
Phosphate rock; f. o. b. mine:				
Florida land pebble, 68 per cent.....	Ton	2.25	@	2.50
Tennessee, 70-80 per cent.....	Ton	5.00	@	5.50
Potassium, "muriate," basis 80 per cent.....	Ton	—	@	—
Pyrites, furnace size, imported.....	Unit	15	@	—
Tankage, high-grade.....	Unit	3.25	@	10



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## TABLE OF CONTENTS

### EDITORIALS:

- On Our Opportunities. . . . . 794  
Resignation of A. M. Patterson, Editor of Chemical Abstracts. . . . . 794

### ORIGINAL PAPERS:

- The Influence of Organic Admixtures on the Setting of Cement. By H. K. Benson, C. A. Newhall and Bailey Tremper. . . . . 795  
The Use of Fine Earth in Mortars. By H. K. Benson and J. S. Herrick. . . . . 796  
Water Purification by Ozone—With Report of the Ann Arbor Plant. By R. W. Pryer. . . . . 797  
Studies on the Absorption of Water by Building Brick. By Hermann W. Mahr. . . . . 800  
Isoprene from Commercial Turpentine. By Chas. H. Herty and J. O. Graham. . . . . 803  
Investigations on Oil of Black Sage. By Charles E. Burke and Charles C. Scalione. . . . . 804  
Examination of Chinese Wood Oil. By E. E. Ware and C. L. Schumann. . . . . 806  
Oils of the Coniferae. II—The Leaf and Twig, and Bark Oils of White Fir. By A. W. Schorger. . . . . 809  
A New Method for the Determination of Zinc in Treated Wood. By M. Hume Bedford and R. Pfanstiel. . . . . 811  
A New Qualitative Test for Silicates in Soap. By Harold W. Leitch. . . . . 811  
Oxidation of Sulfur Compounds of Coal, and of Nitrogen in the Bomb Calorimeter, and the Correction to be Applied in Determining the Heating Value of Coal. By Samuel H. Regester. . . . . 812  
Ethyl Ester of Linolic Tetrabromide as a Product in the Analysis of Cottonseed Oil. By Leroy S. Palmer and Philip A. Wright. . . . . 822  
Enzymes of *Aspergillus Oryzae* and the Application of Its Amylolytic Enzyme to the Fermentation Industry. By Jokichi Takamine. . . . . 824  
Alcohol in the Manufacture of Phosphoric Acid and Phosphates. By Paul J. Fox. . . . . 828  
The Action between Clay Filters and Certain Salt Solutions. By W. B. Hicks. . . . . 829  
Selective Adsorption. By E. G. Parker. . . . . 831  
The Estimation of the Lime Requirement of Soils by Means of the Hydroxide of the Alkaline Earths. By C. R. Moulton and P. F. Trowbridge. . . . . 835  
A Study of the Dolomitic Limestones of the Allentown Quadrangle. By Samuel H. Salisbury, Jr., and George C. Beck. . . . . 837

### LABORATORY AND PLANT:

- Determination of Carbon in Steel by the Direct Combustion Method. By Wm. Brady. . . . . 843  
An Apparatus for the Analysis of Complex Gas Mixtures. By Guy B. Taylor. . . . . 845  
The Instantaneous Thermostat and Smoke and Fume Monitors, Precipitators and Recorders. By W. W. Strong. . . . . 848  
ADDRESSES:  
Air Ozonation. By Milton W. Franklin. . . . . 850  
The Importance of Enzymes and Enzyme Reactions in Medicine and Surgery. By W. G. Lyle and P. A. Kober. . . . . 855

### OBITUARIES:

- William Lofland Dudley. . . . . 856

### CURRENT INDUSTRIAL NEWS:

- Some Phases of the Industrial Situation in Great Britain. . . . . 859  
Alloy-Steel Gears in Machine Tools. . . . . 862  
The United States Coal Output. . . . . 862  
By-Product Coke Ovens in Russia. . . . . 862  
On Accumulator Electrolytes. . . . . 862  
The Fullagar Internal Combustion Engine. . . . . 862

### NOTES AND CORRESPONDENCE:

- Note on the Determination of Cineol. . . . . 863  
The Present Status of the Glass Bottle Industry in the United States. . . . . 864  
The Hydrocarbons of Utah—A Correction. . . . . 865  
Remedies for Potash Shortage. . . . . 866  
Dr. Leo H. Baekeland in Japan. . . . . 866  
American Electrochemical Society. . . . . 867  
American Gas Institute. . . . . 867  
Annual Meeting of the American Chemical Society Called Off. . . . . 868  
Some Economic Aspects of Industrial Chemistry—A Correction. . . . . 868  
PERSONAL NOTES. . . . . 868  
GOVERNMENT PUBLICATIONS. . . . . 869

### BOOK REVIEWS: The Occupational Diseases, their Causation, Symptoms, Treatment and Prevention; The Electrical Conductivity and Ionization Constants of Organic Compounds; Chemistry of Dyeing; The Organometallic Compounds of Zinc and Magnesium; Chemistry and Its Borderland; The Silicates in Chemistry and Commerce. . . . . 871

### NEW PUBLICATIONS. . . . . 875

### RECENT INVENTIONS. . . . . 876

### MARKET REPORT. . . . . 878

## EDITORIALS

### ON OUR OPPORTUNITIES

While the eyes of the world are turned upon the military activities of Europe, business strategists in the United States will not fail to recognize the tempting opportunities offered for making ourselves more independent of foreign supplies.

It must not be assumed, however, that the gaps left in our stocks can be filled by a simple twist of the wrist. We have received hundreds of inquiries as to where this or that chemical may be purchased, who can design and erect a plant for producing some particular product, what concern makes the machinery for some difficult process of manufacture, etc. Many of these letters indicate a distressing lack of knowledge of the problems involved or of the magnitude of the undertakings. Many seem to lose sight of the complicated interlocking of processes and products in the development of manufacture and other equally important considerations. Unless extremely well advised many of the proposed ventures will result in failures.

A great responsibility is now being placed upon our profession by the sudden cessation of the importation of chemical supplies. Chemists and chemical engineers have never been confronted with greater responsibilities nor greater opportunities. Their resourcefulness will be taxed to its limit to prevent serious interruption of some of our industrial processes, and on the other hand, the soundest sort of judgment will be required to avoid the pitfalls of new manufacturing ventures.

Making goods is only one phase of successful manufacture. The war in Europe will soon be over and the impoverished European manufacturer will then compete with even greater severity than in the past. The fickle buyer will lose his fondness for the American manufacturer who tides him over this crisis, just as the public lose their interest in our soldiers and sailors in time of peace. Colleges and laboratories will rush abroad with their orders for glassware and chemicals as they have in the past, as soon as normal conditions are restored. These and many other factors are to be considered in connection with the wholesale advice that now is the time to build great American chemical industries. The ability to build the plants, develop the processes and make the products undoubtedly rests with the American chemists. The investor, however, must be advised of the shoals ahead for the other phases of his enterprise. Public good-will is needed to sustain the efforts and share the risks of the pioneer. A constructive governmental policy wisely administered to conserve these industrial developments is essential and it is hoped that our government will meet its obligation and foster these opportunities. The great advantages of interlocking processes and products in the large foreign manufacturing plants of Europe can be attained in America only by the active coöperation of our manufacturers.

That great opportunities for development and expansion have been forced upon us by the European crisis is recognized by all. The success with which we utilize these advantages will depend not alone upon our technical skill and judgment but upon the coöperation of manufacturing, consuming and governmental interests with a view to stabilizing the new enterprises during their delicate and expensive developmental stages.

### RESIGNATION OF A. M. PATTERSON, EDITOR OF CHEMICAL ABSTRACTS

It is with very great regret that we have to announce the retirement of Dr. Patterson from the editorship of *Chemical Abstracts*, because he has been compelled, for a time, to give up all confining work. Dr. Patterson first joined the staff of *Chemical Abstracts* as Associate Editor in the fall of 1908. He brought to Abstracts a fund of experience gained during several years of work as a scientific editor, and a spirit of devotion to the interests of our Society which have been invaluable. He soon took almost complete charge of the details of management, and a year later the headquarters were moved from Urbana, Illinois, to Columbus, Ohio. Shortly afterwards he was chosen Editor-in-chief. During the four years that followed he so developed and perfected the organization that, in spite of the limited means at its disposal, *Chemical Abstracts* now gives a much more complete record of the world's chemical literature than all other abstract journals combined. This has been accomplished, on the one hand, by the systematic arrangements which have been made to discover all sources of publication of original chemical articles in the world, and on the other by securing a hearty spirit of coöperation and loyalty on the part of assistant editors and abstractors.

During all of this time, with a very limited staff in his office and under the necessity for the most rigid economy in the conduct of Abstracts, Dr. Patterson performed an amount of routine work in the preparation and arrangement of manuscripts for the printer and in the reading of proof which would have seemed impossible to a less faithful and conscientious editor. He also made a careful study of questions of orthography and nomenclature for chemical terms, which has made *Chemical Abstracts* the best authority we have in this field.

Somewhat more than two years ago he assumed other duties which made it necessary for him to drop a large portion of the work which he had been doing, and since then the First Associate Editor, Mr. J. J. Miller, has taken up the details of management and has now come into full executive control as Editor. Mr. Miller has been connected with *Chemical Abstracts* for five years, and we are extremely fortunate in having such an able successor to Dr. Patterson ready to assume the editorial chair.

# ORIGINAL PAPERS

## THE INFLUENCE OF ORGANIC ADMIXTURES ON THE SETTING OF CEMENT

By H. K. BENSON, C. A. NEWHALL AND BAILEY TREMPER

Received July 7, 1914

Specifications governing the use of sand in concrete quite generally prescribe it to be clean, although nu-

merous instances of the use of sand containing clay or silt without injury to the resulting concrete have been cited. Hain,<sup>1</sup> Greisenauer,<sup>2</sup> and C. E. Sherman<sup>3</sup> show

that the presence of organic matter and of clay or loam had little or no effect on the tensile strength of the mortar and in one instance,<sup>1</sup> the claim is made that washing out loam from the sand decreased the tensile strength. The results obtained by Benson and Her-

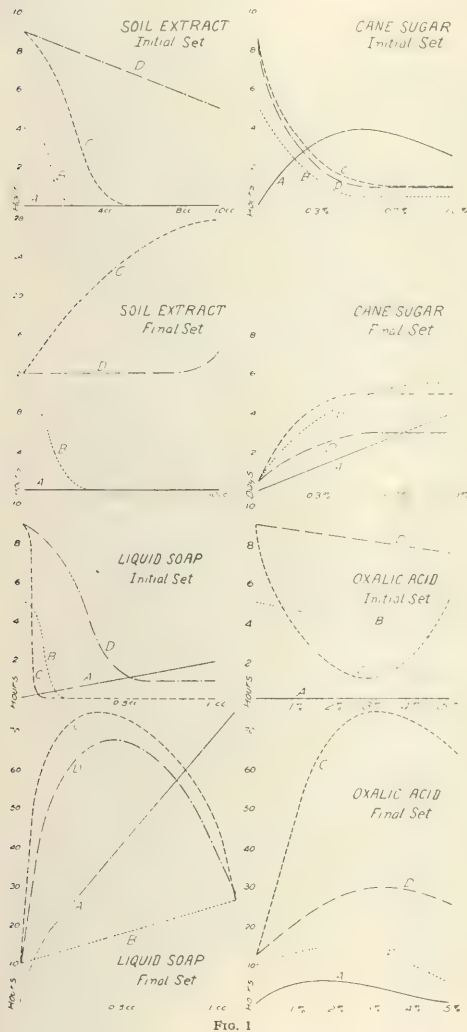


FIG. 1

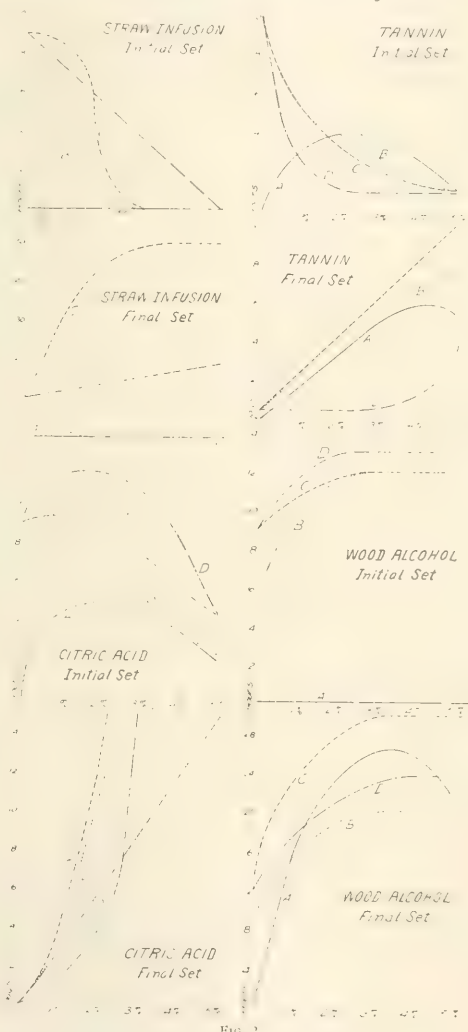


FIG. 2

merous instances of the use of sand containing clay or silt without injury to the resulting concrete have been cited. Hain,<sup>1</sup> Greisenauer,<sup>2</sup> and C. E. Sherman<sup>3</sup> show

steam pressure from fine earth and cement also confirm the statements already cited.

Yet it is known that in cases where a given cement used with a standard sand gave normal results as to

<sup>1</sup> Eng. News, 53 (1905), 127.

<sup>2</sup> Ibid., 51 (1904), 413.

<sup>3</sup> Ibid., 49 (1903), 443.

<sup>1</sup> Eng. News, 49 (1903), 446.

<sup>2</sup> This Journal, 6 (1914), 796.



strength and time of setting, the same cement when used with a so-called "dirty" sand, was greatly retarded in time of setting or did not harden at all. It is of interest to know what foreign constituents in the sand, other than inorganic matter, might be responsible for the failure of the cement to set. Experiments were accordingly undertaken with organic compounds typical of such classes as might be expected to be present in the soil or sand deposits.

Schreiner and Reed<sup>1</sup> state that the subsoil contains on the average 0.83 per cent organic matter, as found in thousands of samples from all parts of the United States. Prominent among these organic compounds are the carbohydrates, proteids and lecithins, which exist in the living cells of plants. During decomposition of the latter, primary and secondary decomposition products may result.

#### EXPERIMENTAL

Samples of cement were prepared from the clinker from two plants (the Olympic brand is made by the wet mix and the Superior by the dry mix process). The medium-sized clinker was screened out for use, crushed and ground in a pebble mill until 99.8 per cent passed the 100-mesh sieve and 80.0 per cent the 200-mesh sieve. Four different samples were prepared, namely, each brand straight and each brand ground with 2½ per cent of gypsum. All samples were used within two weeks after grinding and all were kept in air-tight Mason fruit jars.

In order to carry on the experiment at as nearly constant temperature as possible, the work was done in a concrete basement which contained the moist closet, water and other materials. Standard methods<sup>2</sup> of testing were followed. Instead of following the usual plan of mixing different cements to the same consistency, here the quantity of water necessary for normal consistency was used throughout:

The percentage of water required for A was 26; B, 25; C, 26; D, 23.

The accompanying diagrams show the results of tests made with various percentages of organic compounds, the time of setting being shown in hours. In addition to these substances, admixtures of one-half per cent of the compounds enumerated in Table I were studied.

TABLE I—RETARDATION OF SETTING CEMENT

	A—Olympic straight B—Olympic plus gypsum		C—Superior straight D—Superior plus gypsum	
	A	B	C	D
	Initial	Final	Initial	Final
Asparagine.....	0.00	20.00	2.00	24.00
Cumarine.....	0.01	32.00	6.30	22.00
Glycecol.....	0.01	21.00	3.00	31.00
Isoborneol.....	0.00	21.00	5.00	16.00
Quinoline.....	0.00	13.30	4.30	14.00

#### DISCUSSION

The addition of the various substances in some cases was accompanied by apparent chemical action such as heat liberation, color change and formation of precipitate. The nature of these reactions is indicated in Table II. To ascertain the component of the cement with which such reaction takes place, comparison is made with a calcium salt in solution. If we

accept Richardson's theory that the initial set of cement is due to the decomposition of the calcium aluminates with the accompanying crystallization of calcium hydroxide, then any substance, which can effect the removal of the calcium ion by forming an insoluble precipitate, will be able to hasten the initial set of the mortar. The five substances which react thus are tannin, straw infusion, oxalic acid, quinoline and soap—all greatly accelerated the initial set and all formed precipitates with cement and calcium chloride. These substances also exerted the greatest retarding influence in the final set. If the latter be represented as due to a secondary reaction between the aluminates and calcium hydroxide to form a basic aluminate, as held by Le Chatelier, any substance causing the removal of calcium hydroxide will retard the reaction.

TABLE II—CHEMICAL REACTIONS OF ORGANIC REAGENTS WITH CEMENT AND CALCIUM CHLORIDE

REAGENTS	CEMENT	CALCIUM CHLORIDE
Methyl alcohol	Yellow precipitate	No action
Oxalic acid	Heat liberated	Precipitate
Cane sugar	No action	No action
Citric acid	No action	White precipitate when boiled
Straw infusion	Gray precipitate	Yellow precipitate
Tannic acid	Gray precipitate	Gray precipitate
Liquid soap	Precipitate	Precipitate
Glycecol	Flocculent precipitate	No action
Soil extract	Brown precipitate	No action
Isoborneol	No action	No action
Cumarine	No action	No action
Asparagine	Light precipitate	No action
Quinoline	Precipitate	Precipitate

#### CONCLUSIONS

I—The retarding effect on the setting of cement can not be attributed to any class of compounds.

II Certain organic substances form insoluble compounds with the calcium of cement and these retard the final set.

III—In some cases insoluble compounds were formed with components other than the calcium of the cement and these also exerted a retarding influence but to a less extent.

IV—There is no evidence of catalysis and the action takes place principally by disturbing the equilibrium.

LABORATORY OF INDUSTRIAL CHEMISTRY  
UNIVERSITY OF WASHINGTON  
SEATTLE

#### THE USE OF FINE EARTH IN MORTARS

By H. K. BENSON AND J. S. HERRICK

Received July 7, 1914

In the construction of concrete foundations for paving country roads, sand and gravel are often transported considerable distances. It is evident that much advantage can be derived by using the soil itself if it can be shown that sufficient strength can be developed in mixtures of soil and a suitable binder. A number of experiments were accordingly undertaken and the results, although partial and incomplete, are herewith presented.

The soil of the campus of the University of Washington is described<sup>1</sup> as the Everett gravely sandy loam, is formed from a deep glacial till, and is representative of a large proportion of the Puget Sound Basin. From a cut twelve feet in depth, samples of soil were taken at different levels. Sample No. 1 was a fine sand,

<sup>1</sup> "Reconnaissance Soil Survey of Eastern Part of Puget Sound Basin," Bureau of Soils, U. S. Department of Agriculture.

<sup>1</sup> Bull. 47, Bureau of Soils, U. S. Dept. of Agriculture.

<sup>2</sup> Circ. 33, U. S. Bureau of Standards.

containing considerable clay, taken at the bottom of the cut. Sample No. 2, from the middle of the next stratum, about 4 feet above the bottom of the cut, was very hard and compact in the bank and contained numerous pebbles. Sample No. 3, from the next stratum above, about 6 feet from the bottom of the cut, was stained yellow and was sandy in texture. Sample No. 4, 10 feet from the bottom of the cut, was a yellow loam containing considerable fine material and humus and resembled a typical garden soil in texture and appearance. Sample No. 5, the subsoil, was apparently a decomposed glacial till, having the same color and characteristics as No. 2 but not being hard or difficult to loosen. Sample No. 6 was taken from the surface, formerly a garden, and contained considerable humus. All the samples were air-dried, and passed through a ten-mesh sieve, the residue, comprising 30 to 40 per cent, being discarded.

The analyses of the fine earths thus obtained, together with that of Sample 7, an ordinary mortar sand, are given in Table I.

TABLE I—SIEVE ANALYSIS OF FINE EARTHS  
Percentages passing mesh indicated

Sample No.	200	100	50	40	30	20	10
1.....	77.2	98.0	99.0	All			
2.....	17.0	29.7	64.4	74.3	85.0	90.5	95.6
3.....	6.4	14.3	57.5	69.1	82.7	92.2	All
4.....	10.7	18.7	52.8	65.0	79.8	91.7	All
5.....	17.2	32.5	68.7	79.5	87.8	93.1	All
6.....	14.6	26.8	64.5	76.7	85.5	93.1	All
7.....	0.5	5.0	71.9	90.0	97.5	All	

For the preparation of the mortar from the fine earth and the cementing agent, the general procedure was to mix thoroughly, add 12 per cent water, silo in a moist closet for 24 hours, mold into bricks, 1 in. X 4 in. X 4 in., and press into shape under a hydraulic pressure of 2000 pounds per square inch. These bricks, after air-drying for 24 hours, were then placed in an autoclave and subjected to the action of live steam under 80 pounds pressure for 8 to 16 hours. The bricks were then broken in an Olsen machine, each brick being laid on the flat surface. Tables II and III give the results obtained by the use of various mixes of fine earth and cementing agent.

TABLE II FINE EARTH MIXTURES WITH LIME AND WITH PORTLAND CEMENT

Sample No.	Percentage		Crushing strength Lbs. per sq. in.	Percentage		Crushing strength Lbs. per sq. in.
	Fine earth	Lime		Fine earth	Portland cement	
1	90	10	5497	90	10	3480
	80	20	6200	80	20	6250
2	80	20	3460	70	30	5700
3	90	10	3290	90	10	6250
	80	20	2740	80	20	6250
4	90	10	2540	70	30	5700
	80	20	2440	80	20	6250
5	90	10	3680	90	10	1500
	80	20	2820	80	20	5850
	70	30	4980			
6	90	10	2720	90	10	1940
	80	20	2320	80	20	2920
	70	30	3410	70	30	6070
7	85	15	6200	90	10	4700
				80	20	4800
				70	30	9750

In using Portland cement, siloing of the mixes was of course impracticable, but the other steps were followed as above outlined. Since it has been shown by Acheson and others that soluble organic matter increases the colloidal content of clay, it was believed that soils of loamy character might be advantageously

treated with straw infusion made by boiling oats straw with water and decanting the clear liquid. A quantity of the infusion necessary to produce the maximum plasticity was then incorporated with the lime and fine earth mixtures and the resulting bricks tested. The earths of sandy texture either disintegrated in the autoclave or gave low strength tests while the loamy earths gave a crushing strength of above 3000 lbs. in mixtures containing less than 10 per cent lime. Similar results were obtained with a 2 per cent solution of tannic acid.

To confirm the results given in Table II, new mixtures were made up with varying quantities of lime, the results of which are given in Table III.

TABLE III—LIME—FINE EARTH MIXTURES  
Percentage

Sample No.	Fine earth	Lime	Crushing strength Lbs. per sq. in.
3	90	10	5550
4	85	15	4640
	97.5	2.5	3300
5	92.5	7.5	5820
	95	5.0	6200

### CONCLUSIONS

As the result of this work, it is shown that under the influence of heat and pressure, various fine earth plastics may be hardened to an extent approaching that of concrete. The presence of soluble organic matter does not prevent the hardening of loamy mixtures of fine earth and lime. Furthermore, as small quantities of lime as  $2\frac{1}{2}$  per cent develop considerable strength in the hardened brick.

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### WATER PURIFICATION BY OZONE—WITH REPORT OF THE ANN ARBOR PLANT

By R. W. PRYER  
Received June 13, 1914

The problem of obtaining a safe water supply is one of the greatest questions of the day for many cities. The difficulty of obtaining a pure water in sufficiently large quantities has proved too great for most cities of any considerable size, and compelled them to use a less desirable supply and to purify the same.

A method of purification that has met with some success in several European cities is that of ozonization. Some cities that have all, or part of their water supply purified in this way, are Paris, Lille and Nice in France, Ginnekin in Holland, and St. Petersburg in Russia. In this country there are only a few of these plants, none of them of any great size, and none of them attracting any particular notice as examples of cheap efficient water purification.

In the summer of 1912 a large force of men were at work just above the intake of the Ann Arbor Water Co. plant, building a dam for the Eastern Michigan Edison Co. The situation was very similar to that at Ithaca, New York, at the time of the epidemic of typhoid fever in 1903; with this disastrous experience in mind, these two companies united to avoid, if possible, an epidemic in Ann Arbor.

The major part of the work was done during this

time, while the writer was in the service of these two corporations as sanitary inspector. The usual precautions, such as locating the camps below the intake, having all closets that were above the intake watertight, and having the contents burned below, were taken. The water was plated daily and as soon as the course of the river was turned, hypochlorite of lime was used in large amounts. It is indeed gratifying to report that not a single case of typhoid fever, that could be in any way laid to the water, developed during this time.

#### WATER SUPPLY

The water that is treated at the Ann Arbor plant is taken from the Huron River about two miles above the city. The source of the river is in a chain of lakes twenty to thirty miles, by river, from this place. The river is comparatively free from contamination by man, but as the valley of the river and its tributaries are much used for grazing purposes, chances for contamination from animals are exceedingly good. Indeed the writer has pictures showing thirty-five head of cattle wading in the river less than one mile above the intake.

The water is pumped from the river to a roughing filter located on a hillside back of, and above, the pumping station. This filter is 30 ft. square and consists of about 5 ft. of sea sand. Head of water on filter is from 4 to 5 ft. The filter is washed frequently by reversing the flow of the water.

From the filter the water flows by gravity to the bottom of the fore bay, a single compartment just in front of the rear bays. From this fore bay the water flows through regulating valves into the rear bays, which are three separate compartments located in front of the first well of each unit. Concrete construction is used throughout.

#### STERILIZING WELLS

These wells are from 8 to 9 ft. from water level to the bottom, and are arranged in step-like formation, the bottom of each being about 5 ft. lower than that of the one before. There are three of these wells in each unit and three units in all. The water flows from the rear bays, through pipes, to the bottom of the first well, rises through, flows over and through pipes to the bottom of the second well and similarly from the second to the third. The openings from the third well lead directly into the pumping basin. The ozonized air under from 5 to 8 lbs. pressure is forced up through each well, which is divided into two sections by baffling plates consisting of a metallic screen covered with small pebbles to a depth of about 6 in.

#### TYPE OF OZONIZER USED

The ozonizer in use is very similar to the Siemens-De Frise type, some of the differences being the use of an outer aluminum pole, substitution of mica tubes for a glass dielectric and the absence of a water jacket for cooling purposes.

The outer aluminum pole is fastened in an iron casing and is grounded, while the inner aluminum pole is insulated away from the casing and is connected

directly to the transformer. Between these aluminum poles are the mica dielectrics, and the space between the dielectrics and the aluminum poles is about  $\frac{1}{16}$  in. There are 109 sets of tubes in each ozonizer, and three ozonizers are used. When the current is turned through the ozonizer, the discharge takes place through the mica tubes, and is what is known as the silent or brush discharge, characterized by a peculiar bluish violet radiation.

A 110 volt alternating current generator furnishes the power, which is stepped up by transformers to from 11,000 to 12,000 volts.

A steam-driven air compressor forces air, under from 5 to 8 lbs. pressure, through the space around

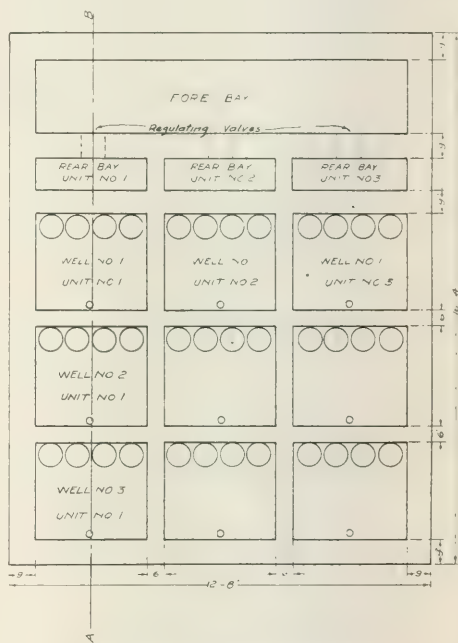


PLATE I ARRANGEMENT OF OZONIZING WELLS

the mica dielectrics, where it is ozonized, and from there to the bottom of the sterilizing wells.

#### OZONE CONTENT OF AIR AND VOLUME RATIO OF OZONIZED AIR TO WATER

The average of several determinations of ozone in the ozonized air shows that the amount of actual ozone averages about 0.5 gram per cubic meter, the lowest amount found being 0.384 gram, and the highest amount being 0.705 gram. It should be said, however, that when the amount of ozone was found to be 0.705, the voltage on the circuit from the generator was 125, indicating a voltage of 12,500 in the ozonizers. This is higher than is usually carried and indeed higher than can be carried without constant danger of breakage. The amount of water passing through the ozonizing wells per hour is calculated to be 50,000 gallons, or 189.4 cubic meters. The amount of ozo-



nized air varies somewhat, but the maximum amount observed by the writer was 85.4 cubic meters per hour. This makes the ratio of ozonized air to water 1 : 2.2 and the amount of actual ozone averages 0.227 gram per cubic meter of water, or is 0.227 part per million.

The comparison of the ozone content and the volume ratio of ozonized air to water at this plant, with the figures from some other plants, presents an interesting contrast.

Plant at	Ozone content Grams per cubic meter of air	Ratio of ozonized air to water
Saint Maur.....	2.0	3 : 4
Nice.....	2.591	1 : 4
St. Petersburg.....	2.5	4 : 1
Ann Arbor.....	0.5	1 : 2.2

#### COST OF OPERATION

The exact cost of operating this plant is rather difficult to obtain, owing to its close connection with the

per cent per year. This makes a total operating cost of approximately \$9.90 per million gallons. As ordinarily operated, one million gallons pass through in 20 hours. Estimates of the operating costs per million gallons for several other ozone plants are as follows: St. Maur, \$15.60; Ginnekin, \$20.00; Howard-Bridge System, \$16.80 (estimate for 10,000,000 gallon plant, \$7.20); Estimate for 20,000,000 gallon plant for Paris, \$8.00.

#### BACTERICIDAL ACTION

The writer has tested this plant frequently during the last two years, and at no time has found any considerable reduction in the bacterial count between the ozonized and the filtered water; indeed, usually more bacteria were found in the ozonized than in the filtered water. Possible reasons for this will be considered later.

The results as shown in the tables below were obtained with the ozonizing wells as described in the first part of this article. Several changes have been made in the arrangement and operation of these wells, and they were tested out thoroughly with no noticeable improvement as regards bactericidal action.

The first change made was to turn all the ozone through wells No. 1 and No. 2 of each unit. The second to cut out one unit entirely and turn all the ozone through wells No. 1 and No. 2 of units No. 1 and No. 2. No apparent benefit resulted from these changes, however, and the tables give one a fair idea of the action of the filter alone and of the filter and ozone combined. These tables show the total number of organisms found per cc. on standard nutrient agar after 48 hours at 37° C.

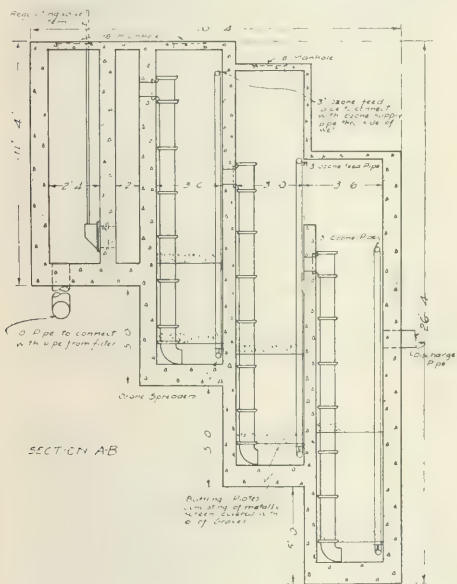


PLATE II—CROSS SECTION OF OZONIZING WELLS

rest of the system, and these figures must be regarded as an estimation only. This estimate does not include the cost of pumping from the river, as it is assumed that this would be done whether the ozone plant were operated or not.

For the production of the electrical energy about 12 H. P. are required, while the air compressor is estimated to require 7 H. P. On the assumption that 1 H. P. per hour requires 4 lbs. of coal, this would make the operating cost for coal alone, approximately \$1.90 per million gallons. Oil packing repairs, etc., total to about \$1.44 per million gallons. To this must be added \$6.56 to cover interest on investment, calculated at 5 per cent, taxes and insurance, calculated at prevailing rates, and depreciation calculated at 4

		NO. OF BACTERIA IN WATER		
Aug. 15, 1912		Raw	Filtered	Ozonized
9 A.M.	650	560	620	
11 A.M.	440	300	220	
1 P.M.	370	190	160	
Filter washed at 2.30 P.M.				
3 P.M.	700	480	710	
5 P.M.	460	170	210	
7 P.M.	350	120	140	
9 P.M.	580	270	310	
Aug. 27, 1912				
9 A.M.	450	70	220	
10 A.M.	480	180	120	
11 A.M.	420	90	120	
12 M.	280	200	140	
1 P.M.	520	150	160	
2 P.M.	460	140	130	
3 P.M.	340	140	130	
4 P.M.	610	180	170	
5 P.M.	200	130	210	
6 P.M.	320	120	150	
7 P.M.	410	220	180	
8 P.M.	460	130	120	
Filter was washed at 8.30 A.M.				
Nov. 23, 1912				
10.30 A.M.	240	200	120	
12.30 P.M.	160	110	60	
3.45 P.M.	140	60	30	
5.45 P.M.	160	20	30	
8.30 P.M.	70	40	160	
9.30 P.M.	300	120	90	
Average of 25 samples		382+	173+	188-

Particular attention was paid during this time to presumptive tests for the colon germ. During the summer this organism was only occasionally found in the river water and very rarely found past the filter. However, on Nov. 23, 1912, and many times since, many acid-producing colonies were found on the writer's plates of the water made with Conradi-Drigalski media, and these seemed to be practically as numerous in the ozonized as in the filtered water. Many of these acid-producing colonies have been

tested out in pure culture, and the fact that *B. coli* can go through the ozonizing wells has been proven beyond a doubt.

As an explanation of the negative efficiency of the ozone considered alone, I might state that the bottom of the third well of each unit is lower than the height of water in the pumping when full. Consequently, these third wells are flooded with basin water, and as this is open and located near a railroad, it is liable to receive more or less contamination. This is the explanation advanced by some; but each day, during the entire time that the writer was taking samples, the water in the basin was low, and consequently no basin water could get back into these wells. It would seem that they would gradually sterilize themselves if the ozone were present in large enough quantities to have any beneficial action on the water in them, but samples taken after ten hours' continual operation, during which time no basin water could get into these wells, showed no improvement in the ozonized water.

Another explanation of this negative efficiency, advanced by Dr. F. G. Novy, professor of bacteriology in the University of Michigan, is as follows: a microscopical particle of organic matter may contain several bacteria and still appear as one colony and be counted as an individual. Now this ozonized air tears through the water under several pounds pressure, and it is probable that some of these particles of organic matter, containing germs, are broken into several sections and give several colonies, whereas they all showed as one colony in the raw or filtered water.

In the summer of 1912 a large dam was built just above the former intake of the water company. As the manager of this company wished to be absolutely sure of the quality of the water supplied to the city, the use of hypochlorite of lime was begun. Plate counts of the tap water in the city are made every day and the amount of lime is varied to suit the requirements. At the present time the intake is above this dam, and as the water is backed up for nearly two miles, a very good settling basin is formed. This water contains considerable organic matter and the amount of hypochlorite used is rather high, from 10 to 16 lbs. per million gallons. The percentage of available chlorine in this averages about 33 1/3 per cent, thus making the available chlorine used come to an average of about 0.5 part per million. Even with this comparatively high amount of hypochlorite, the germ count in the service water will average more than 50 per cc. However, the colon bacillus is rarely found.

Now chlorine is much more soluble in water than is ozone, and gram for gram is as strong, if not a stronger, disinfecting agent. Consequently, the fallacy of trying to purify a water with 0.227 part per million of ozone, when the water is comparatively rich in organic matter, and when 0.5 part per million of available chlorine does not give ideal results, must be plain to all.

The writer wishes to thank Dr. A. K. Hale, of the Ann Arbor Water Co., for his many favors. The

writer desires also to thank Dr. V. C. Vaughan and Dr. F. G. Novy, of the University of Michigan, and Mr. Gardner S. Williams for their many helpful suggestions.

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## STUDIES ON THE ABSORPTION OF WATER BY BUILDING BRICK

By HERMANN W. MAHR

Received July 2, 1914

The absorption of water by building brick has probably been given more attention than all the other properties of this important construction material. We are, however, still in doubt as to the best method of conducting the test for absorptive power. Attempts to explain the significance of the amount of water taken up and the relation of this value to the strength of the material have been unavailing. Howard<sup>1</sup> has presented papers pointing out the indefiniteness of the term absorption as applied to brick. In spite of this confusion, the absorption requirement is regarded as of importance in judging quality, apparently because of a well-grounded belief that future investigations would open up this dark continent.

Some experimenters have attempted to evolve absorption test methods which give total porosity, and the standard method of The American Society for Testing Materials, proposed in 1913, has this object in view. It has been pointed out by several authorities, among them J. C. Jones,<sup>2</sup> that no constant relation exists between the absorptive power and porosity of bricks. We are, therefore, forced to conclude that the two are distinct properties having some small dependence on one another. Investigations of absorption of water have been mainly from the exterior of the brick, and these have failed to answer many queries. Necessarily the structure of the brick holds these secrets.

To investigate the structure of bricks as revealed by the absorption test and the significance of the latter, a study of these materials was undertaken. The bricks employed were of different degrees of burning and were submitted by Hudson River and New Jersey manufacturers. Previous to immersion they were dried for 24 hours at 110° C. They were then subjected to absorption tests, either the 48 hours' total immersion or the boiling test proposed by a committee of The American Society for Testing Materials in 1913.<sup>3</sup> The immersion liquid was a 2 per cent solution of potassium ferrocyanide. At the close of the test superficial moisture was removed and weights determined. The bricks were then split across (or lengthwise), into sections, by means of a brick chisel. The surfaces thus obtained were treated with a 5 per cent solution of ferric chloride. When the section was dried the zones and channels of penetration by the liquid were colored blue. The two surfaces from the same fracture showed markings in practically all instances

<sup>1</sup> National Brick Manufacturers' Association, Buffalo Meeting, February 5, 1909.

<sup>2</sup> Trans. Amer. Cer. Soc., 9.

<sup>3</sup> Proc. Amer. Soc. for Testing Materials, 13 (1913), 287.

the same. This indicated that the coloring was definite and characteristic of the penetration at that place, and not due to flowing of the absorbed solution on the fractured surfaces or other chance phenomena. In some cases splintering of the brick at the surfaces, due to the operation of cutting, gave colorings and zones somewhat different on the two adjoining surfaces.

The procedure just outlined gave well-defined pictures of the penetrated sections; the coloring was, however, not deep and did not contrast as sharply with the unpenetrated parts as when the following treatment was employed. After cutting, the sections were placed in an oven at 110° C. and dried one-half to one hour. The potassium ferrocyanide was thus concentrated on

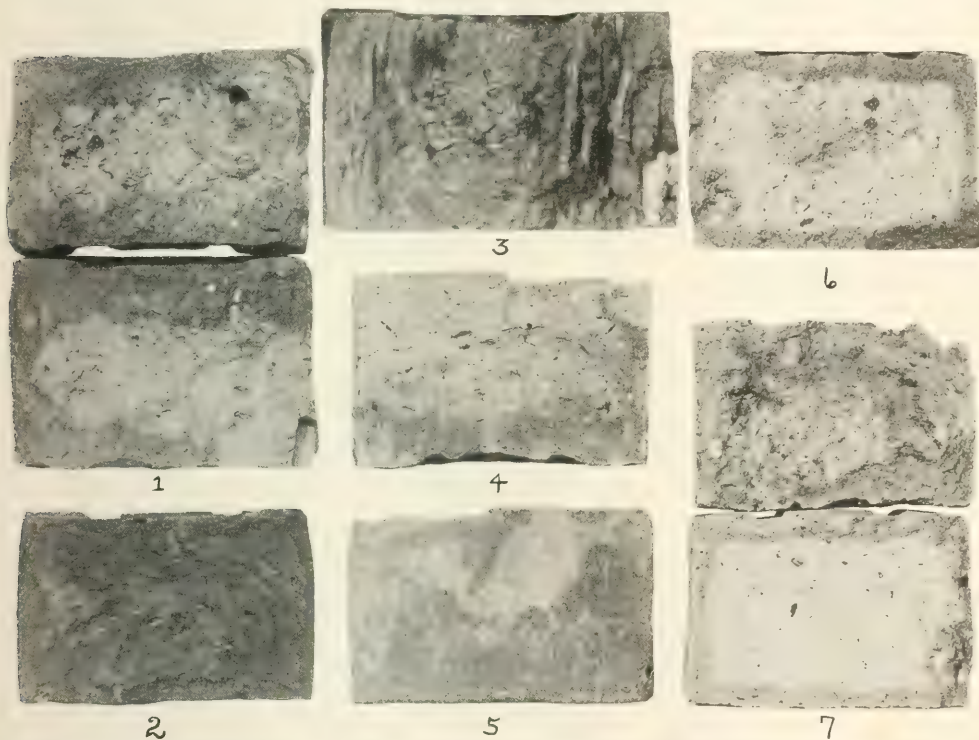
TABLE I—BOILING TEST ACCORDING TO PROPOSED METHOD OF A. S. T. M.

Sample	Percentage absorption in water, by weight	Percentage absorption by weight in 2% potassium ferrocyanide solution
41-2	22.1	21.3
41-31	14.4	18.2
45-1	28.7	27.0
45-23	18.3	16.2
59-5	18.9	16.7

TABLE II FORTY-EIGHT HOURS TOTAL IMMERSION TEST

Sample	Percentage absorption in water, by weight	Percentage absorption by weight in 2% potassium ferrocyanide solution
42-1	18.1	18.2
42-13	11.0	11.3
44-21	14.1	12.4
44-31	14.7	14.5

The results were illuminating and revealed the structure considerably better than breaking the un-



the surface of the penetrated parts. They were then dipped into the ferric chloride solution, dried and washed well. The washing removed the excess of salts and intensified the marking. This method<sup>1</sup> was adopted for the treatment of the bricks hereafter described.

The amount of absorption in 2 per cent potassium ferrocyanide was practically the same for both the 48 hours immersion and boiling tests as when pure water was used. This will be seen from the following tables:

<sup>1</sup> Mr. Gilbert Rigg (*J. Soc. Chem. Ind.*, **33**, 619—June 30, 1914) has very recently described a method, somewhat similar in principle to the above, which he used in studying fire-brick. His method consisted in allowing colored gelatin solutions to penetrate the refractories, and had for its object the revealing of the method and form in which fire-brick would be penetrated by molten slag.

treated brick and visual examination are able to. Some of the grosser defects and variations in composition are shown by the latter, but the method in question showed vitrified and soft portions which are indistinguishable in the untreated brick.

Some of the results illustrative of the penetration into various types of bricks were photographically reproduced. The photographs fall far short of presenting the finer lines and areas of penetration, because of the irregularity of the fractured surfaces and contrasts poorly suited for photographing.

Fig. 1 represents opposite surfaces from the same fracture, the sections being in the position of having



been folded open. This shows the great similarity of the markings obtained on such surfaces.

Fig. 2 is a photograph of a soft absorbent brick subjected to the treatment. The absorption was 18.2 per cent in forty-eight hours total immersion. The penetration was complete at this point. At other places it was not as thorough.

Fig. 3 shows the manner in which a hard, vitreous brick absorbed the liquid. This absorption was only 6.5 per cent. The liquid entered into small channels and soft absorbent zones.

The method in which the liquid penetrated a brick with a hard vitreous core is shown in Fig. 4. The penetration was even in character to the core. This brick absorbed 12.4 per cent. Some of these non-absorbent cores extended the entire length of the brick and their presence on the outside surface was shown by the treatment. Fig. 5, a photograph of the end surface of the preceding brick, shows an instance of this.

A brick, with a large black core, which has been subjected to the absorption test, is shown in Fig. 6. This brick took up only 4.1 per cent. The core, while un-

way they had been penetrated, the exception being soft absorbent bricks which were penetrated evenly and apparently to the same extent by both methods of treatment. Half bricks containing vitreous cores were penetrated only to the core as a result of the 48 hours immersion, while the cores were more or less permeated with liquid by the boiling operation.

In Fig. 7 the lower section is from a half brick which was totally immersed for 48 hours. The upper is a section from the other half of the same brick, subjected to the boiling test. They both contained the same core, but it was penetrated by the liquid as a result of boiling. The absorption by the latter treatment was 12.1 per cent against 4.1 per cent in the half immersed at ordinary temperature.

The results of the experiments lead to several conclusions regarding the methods in which liquids penetrate building brick. The manner of penetration is primarily governed by the type and structure of the brick. The following generalities have resulted from the studies made:

1—Soft, uniform, absorbent bricks take up water uniformly and distribute it evenly to all parts of their

TABLE III EXPERIMENTS ON ACCURACY OF WATER ABSORPTION TESTS

SAMPLE	48 HOURS TOTAL IMMERSION AT ROOM TEMPERATURE										AMERICAN SOCIETY FOR TESTING MATERIALS BOILING METHOD									
	Percentage moisture absorbed					Deviations from mean					Percentage moisture absorbed					Deviations from mean				
	Test 1	Test 2	Test 3	MEAN		Test 1	Test 2	Test 3	AVERAGE		Test 1	Test 2	Test 3	MEAN		Test 1	Test 2	Test 3	AVERAGE	
	1	2	3			1	2	3			1	2	3			1	2	3		
40-12....	18.14	18.39	19.15	18.56		0.42	0.17	0.59	0.39		19.67	19.08	19.71	19.61	19.52	0.52	0.44	0.19	0.09	0.22
40-22....	15.94	15.94	15.94	15.94		0.00	0.00	0.00	0.00		17.09	16.33	17.28	17.09	16.95	0.14	0.62	0.33	0.14	0.41
41-31....	12.88	12.54	12.88	12.77		0.11	0.23	0.11	0.15		13.77	15.00	14.42	14.40		0.63	0.60	0.02	0.00	0.42
42-1....	18.05	15.99	15.93	15.99		0.06	0.00	0.00	0.06		20.98	19.46	21.23	20.86	20.63	0.35	1.17	0.60	0.23	0.39
42-13....	10.78	9.44	10.35	10.19		0.59	0.75	0.16	0.50		14.11	12.97	14.11	13.87	13.77	0.35	0.80	0.35	0.10	0.40
43-1....	17.05	16.93	16.35	16.84		0.21	0.09	0.29	0.20		19.23	17.78	19.54	18.65	18.80	0.43	1.02	0.74	0.15	0.68
44-24....	12.85	13.50	13.14	13.16		0.31	0.34	0.02	0.22		14.45	14.38	15.67	15.18	14.97	0.52	0.59	0.70	0.41	0.55
44-31....	14.44	13.79	13.85	14.03		0.41	0.24	0.18	0.27		15.94	14.75	15.28	15.65	15.40	0.54	0.65	0.12	0.25	0.39
45-1....	21.38	21.20	20.93	21.17		0.21	0.03	0.24	0.16		25.64	24.95	26.42	25.91	25.73	0.09	0.78	0.69	0.18	0.40
45-23....	12.73	12.46	12.73	12.64		0.09	0.18	0.09	0.12		14.80	13.87	16.08	16.57	15.33	0.53	1.46	0.75	1.24	1.00

Average deviation from the mean for method..... 0.21

penetrated, appears to be quite soft. The brick is apparently one which while having a very low absorption, has also low mechanical strength.

In order to compare the effect of the penetration by the boiling test and by the forty-eight hours total immersion, we proceeded as follows:

A number of bricks were cut into halves and the large openings in the fractured surfaces stopped with putty. These faces were then given two coats of shellac varnish, each coating followed by a baking at 110° C. A coat of good spar varnish and another baking completed the treatment, which was designed to prevent absorption through any but the natural external surfaces of the brick. One-half of each brick was then subjected to the boiling test of the American Society for Testing Materials, in potassium ferrocyanide solution, and the other half to the 48 hours total immersion in the same medium.

The halves absorbed approximately the same amounts as the whole brick did when subjected to the same test. Since the ends of the brick may differ in absorptive capacity, exact agreement with results obtained on the whole brick is not to be expected. The half which was boiled showed the usual increase in absorption percentage over the other half which was immersed for 48 hours.

After treatment with ferric chloride the halves of the same brick showed considerable differences in the

structure. This is true for both the 48 hours total immersion and the boiling tests.

2—Hard, vitrified bricks are penetrated only through channels and small absorbent zones by the 48 hours immersion. The boiling test opens up more of the channels, but no large sections of bricks of this class are uniformly penetrated.

3—Bricks containing hard vitrified cores are penetrated to the latter when merely immersed. These cores are well defined and the penetration apparently takes place naturally to the core. Boiling forces the water into these cores to a greater or less extent.

4—An important reason for the lack of definite relation between the absorption and porosity is the existence in some bricks of highly porous cores which are impenetrable in the ordinary immersion test. The absorption test has, therefore, many points of view from which it should be regarded and interpreted.

5—The 48 hours total immersion test fails to penetrate hard cores and apparently gives results which are more indicative of the natural absorptive capacity than the boiling test.

The assumption that the 48 hours total immersion is a measure of the true natural absorption value has been borne out by another set of experiments.

A number of bricks were three times subjected to the 48 hours total immersion test, and the same bricks were likewise subjected to the boiling test of The American Society for Testing Materials a number of times. The

results are given in Table III. In relation to these tests it may be cited that Douty and Beebe<sup>1</sup> have found that no change in the absorption value was caused by repeated dryings and immersions.

The mean results for each brick by each method were then calculated. Similarly the deviation of each result from the mean absorption for the brick by each method was obtained. The latter are given in the columns marked "Deviations from mean." The average deviation from the mean for each brick is also listed under the preceding heading. The average of the latter for all the bricks is a measure of the accuracy with which the test can be carried out. The average deviation for the 48 hours immersion is 0.21 per cent and for the boiling test 0.51 per cent. The balance used for weighing the bricks was accurate to a gram. The constant error due to weighing is, therefore, about 0.06 per cent and is the same for both methods.

With the same instruments and care, results more than twice as concordant may be obtained by the 48 hours total immersion test than by the boiling test. The former being more accurate and uniform in indications is better adapted for contractual testing. The 48 hours total immersion test at ordinary temperatures gives absorption values which uniformly and readily approach the same figure. This is apparently a substantiation of the theory that the absorption by this method is that natural and characteristic of the brick.

STANDARD TESTING LABORATORY  
BOARD OF ESTIMATE AND APPORTIONMENT  
NEW YORK CITY

### ISOPRENE FROM COMMERCIAL TURPENTINES<sup>2</sup>

By CHAS. H. HERTY AND J. O. GRAHAM  
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In connection with the studies of rubber made by polymerization of isoprene, Harries and Gottlob<sup>3</sup> described a method for the preparation of isoprene from spirits of turpentine by means of the "isoprene lamp." In this method the spirits of turpentine is boiled in a flask, in which, just below the neck, is suspended an electrically heated platinum wire coiled somewhat like the filament of a tantalum incandescent bulb. A part of the vapors are decomposed as they pass upward across the heated wire. The flask is attached to an upright condenser maintained at a temperature of 50° C., for condensing the unchanged vapors of spirits of turpentine. The upright condenser is connected with an inclined condenser fed with tap water and this in turn is connected with a receiver surrounded by a freezing mixture. The crude product collected in this receiver is fractionated and the isoprene collected as the fraction boiling between 35° and 37° C.

With this apparatus, Harries and Gottlob obtained a yield of only 1 per cent of isoprene from commercial pinene as against 30 to 50 per cent from commercial limonene. They, therefore, concluded that the yield of isoprene from spirits of turpentine is due chiefly to the presence of dipentene (limonene).

In view of the general interest in the production of rubber from isoprene, it seemed desirable to extend these studies to commercial products closely related to spirits of turpentine and to test further the point mentioned above as to the origin of the isoprene from spirits of turpentine. Accordingly, studies have been made using commercial spirits of turpentine, fractions of the same, pine oil, the volatile oil of *Pinus serotina* (pond pine) and refined spruce pine turpentine.

The apparatus used closely resembled that of Harries and Gottlob, short-circuiting of the sections of red hot platinum wire being prevented by winding the wire on a pipe stem triangular prism. A constant current of 2.25 amperes maintained an even temperature of the wires at a red glow. The flask containing the turpentine was heated by means of a bath of cottonseed oil containing a thermometer. The receiving vessel in the freezing mixture, salt and ice, was a small sulfurous acid condenser. The crude products were refined by distillation through a Hempel column filled with glass beads. The yield of pure isoprene in each of the experiments which follow represents the fraction collected between 35° and 37° C.

#### SPIRITS OF TURPENTINE

200 cc. of spirits of turpentine were boiled in the isoprene lamp until condensation ceased in the inclined condenser. At two-hour intervals the crude product was removed from the receiver and fractionated. Following this experiment, similar experiments were conducted with 200 cc. fractions of spirits of turpentine obtained by fractionation by means of a Young's still head. The first fraction was collected between 155° and 156° C., the pinene fraction; the second, between 169° and 175° C.; the third fraction from 175° C., up. These two last fractions should include the dipentene content of the original spirits of turpentine.

The heating of the two last fractions was continued only two hours, as after that time no further condensation could be observed in the inclined condenser.

The results of the three experiments are shown in Table I.

TABLE I

Substance used	Time of heating Hrs.	Temperature of oil bath	Volume of Crude Cc.	Volume of distillate Refined Cc.	Per cent of isoprene	Volume of residue in heating flask Cc.
Spirits of turpentine..	2	175°	17	6.5	3.25	...
	2	175°	12	3.5	1.75	...
	2	185°	8	1.0	0.50	103
Totals . . . . .	6		37	11.0	5.50	103
Fraction 155°-156°	2	175°	10	6	3.00	...
	2	175°	6	4	2.00	...
	2	175°	4	1	0.50	...
Totals . . . . .	8		20	16	8.00	50
Fraction 169°-175°.....	2	180°	6.5	1	0.50	192
	2	185°	3.25	0	0.00	198

From the direct proof thus obtained it is evident that the yield of isoprene from spirits of turpentine is due to pinene, rather than to dipentene as claimed by Harries and Gottlob.

#### THE VOLATILE OIL OF *PINUS SEROTINA*

This substance has been studied by Herty and Dickson<sup>1</sup> and was found to be particularly rich in

<sup>1</sup> *Proc. Amer. Soc. for Testing Material*, **11**, 770.

<sup>2</sup> Presented at the 48th Meeting of the American Chemical Society, Rochester, September 8-12, 1913.

<sup>3</sup> *Ann.*, **383**, 228.

<sup>1</sup> *J. Am. Chem. Soc.*, **30**, 872.

limonene. Since Harries and Gottlob obtained 30 to 50 per cent of isoprene from commercial limonene with the isoprene lamp, it seemed desirable to study this volatile oil and compare its yield with that from ordinary spirits of turpentine.

In preparing the material from the oleoresin the difficulties formerly met with in distillation by a current of superheated steam were easily overcome by heating the oleoresin at a pressure of one millimeter, the volatile oil readily passing off without any tendency to froth in the flask and with largely decreased opportunity for polymerization during distillation. Table II gives the results with the isoprene lamp.

TABLE II

Substance used	Time of heating, Hrs.	Temperature of oil bath	Volume of distillate		Per cent of isoprene	Volume of residue in heating flask, Cc.
			Crude Cc.	Refined Cc.		
200 cc. of volatile oil of <i>Pinus strobus</i>	2	175°	6.50	5.0	2.5	
	2	175°	4.75	3.0	1.5	
	2	185°	11.00	8.0	4.0	
	2	185°	11.00	8.0	4.0	25.0
Totals	9.0		33.25	24.0	12.0	25.0

No further condensate could be obtained by continued heating of the residue. As was to be expected the yield of isoprene from this volatile oil, rich in limonene, shows a largely increased yield, practically doubled, as compared with ordinary spirits of turpentine.

## PINE OIL

When resinous pine wood is finely divided and treated with steam a crude oil distills off which on fractionation yields wood spirits of turpentine and pine oil. Teeple<sup>1</sup> has found that pine oil consists chiefly of  $\alpha$ -terpineol. The specimen used in this work showed at 15° C. a specific gravity of 0.9403 and an index of refraction of 1.4901. The results with the isoprene lamp are given in Table III.

TABLE III

Substance used	Time of heating, Hrs.	Temperature of oil bath	Volume of distillate		Per cent of isoprene	Volume of residue, Cc.
			Crude Cc.	Refined Cc.		
200 cc. of pine oil	2	210°	15	4	2.0	
	2	210°	10	3	1.5	
	2	210°	7	1	0.5	12.5
Totals	6		32	8	4.0	12.5

## REFINED SPRUCE PINE TURPENTINE

This substance, consisting chiefly of cymene, is collected as a by-product in blowing off the digesters in the manufacture of wood pulp from spruce pine. The specimen was furnished by the A. D. Little Laboratory of Boston. It showed at 15° C. a specific gravity of 0.8639 and an index of refraction of 1.4916; 80 per cent distilled between 171.3° and 174.9° C.; 200 cc. of this substance were boiled three hours in the isoprene lamp but no crude distillate could be observed.

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## INVESTIGATIONS ON OIL OF BLACK SAGE

By CHARLES E. BURKE AND CHARLES C. SCALDINO

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In 1912 a bulletin was published by the Bureau of  
J. Ind. Eng. Chem., 30, 413.

Plant Industry (No. 235), reporting an analysis of the oil of black sage, *Ramona Stachyoides*, of Southern California. This analysis accounted for 62.5 per cent of the oil (camphor, 40 per cent; cineol, 22.5 per cent), but the other constituents were not definitely identified.

Since the black sage grows extensively in Southern California and might become of more or less commercial importance, it seemed to us advisable to continue this work, first with the idea of determining the yields of camphor and cineol at a slightly different season of the year; secondly, to definitely determine the other constituents, and whether or not any of the constituents were present in sufficient quantity to be commercially important.

Through the kindness of Professor C. S. Milliken, Assistant Superintendent of University Extension of Agriculture, several hundred pounds of leaves and twigs which had been simply snipped from the ends of the branches, were forwarded to us from the University Experiment Station at Riverside, in February. These were several weeks in transit and probably suffered some loss from exposure but upon distillation with steam gave a yield of oil corresponding to 0.90 per cent of the weight of material used. This yield is very much higher than that obtained by the Bureau of Plant Industry, who made their distillation about two months later in the season, while the plant was in bloom, and obtained a yield of only 0.75 per cent.

Not only was the yield much greater, but, as might be expected, the physical constants of the oil were quite different from those obtained by the Bureau of Plant Industry, as may be seen from the following comparison:

	Bureau of Plant Industry	Our determination
Specific gravity.....	24° 0.9144	15° 0.8979
Index of refraction.....	30.2 1.4682	24.4 1.4729
Sol. in 70 per cent alcohol....	Sol. in 1 1/2 to 3 1/2 vol.	Insoluble
Acid No.....	2.5	1.6
Ester No.....	2.5	1.6
On cooling to -20° C.....	Solid separated	No solid separated

In order to determine approximately the number of constituents in the oil and the relative quantities of each, we adopted a method which has been successfully used by L. F. Hawley in "Wood Turpentine" (*Forest Service Bulletin, No. 105*). This method consists in fractionally distilling the oil with a Hempel column and plotting curves as follows:

(a) Temperature of distillation against the percentage weight which the fraction distilling at that temperature bears to the total.

(b) Specific gravity against percentage weight.

(c) Index of refraction against percentage weight. *Bulletin 105*, Forest Service, gives approximately the following interpretation of these curves.

Suppose we are dealing with two volatile, miscible components (A) and (B), having boiling points T and T<sub>1</sub>, respectively. (A) and (B) are each present to the extent of 50 per cent. If (A) had no effect on (B) then all of (A) would distil over before any of (B) began to come over, and plotting the percentage distillate against boiling points the two vertical lines AX and BY would result. The break in the curve would indicate a change of composition. In an actual distillation this complete separation is never obtained, one component



affecting the boiling point of the other. The curve obtained when an ordinary mixture is distilled is represented by Curve I where there is a gradual gradation of the two components. A better separation is obtained by the use of a fractionating column and such separation would be represented by Curve II. In general, approaching the vertical indicates a fairly constant composition, a change towards the horizontal indicates a rapid change of composition. Placing this interpretation upon it, Curve II would represent 45

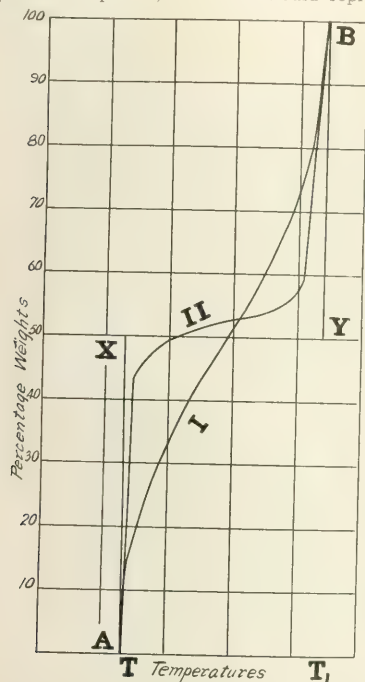


FIG. I—CURVES ILLUSTRATING THE THEORY OF FRACTIONAL DISTILLATION

per cent pure (A), 10 per cent rapidly changing, mixture, and the rest pure (B). In a like manner, the curves obtained from the specific gravity and index of refraction (two of the most constant properties of any oil) should be considered. A rapid change of the specific gravity or index of refraction indicates a rapid change of composition.

TABLE I—FRACTIONATION OF SAGE OIL SHOWING PHYSICAL PROPERTIES OF EACH FRACTION

Fraction	Temperatures C.	Per cent distilled over	Specific gravity 15° C.	Specific Rotation 15° C.	Index of refraction 15° C.
1.....	150-160	5.1	0.878	23.9	1.4616
2.....	160-170	1.9	0.892	23.2	1.4619
3.....	170-175	18.6	0.896	23.3	1.4622
4.....	175-180	17.3	0.914	22.3	1.4626
5.....	180-183	6.8	0.926	20.5	1.4633
6.....	183-186	9.3	0.936	21.2	1.4643
7.....	186-195	3.3	0.939	25.9	1.4646
8.....	195-200	6.1	0.930	(a)	(a)
9.....	200-205	18.6	0.940		
10	Over 205	12.4			

(a) Optical constants not taken, due to formation of solid particles

Table I shows the fractions we obtained from oil of black sage with the constants for each fraction.

Fraction 1 had a pinene-like odor, Fractions 2-7 had a cineol odor, and the rest of the fractions a camphoraceous odor. A small amount of solid matter began to form in the condenser in Fraction 8 as the 200° mark was reached; this solid matter collected so rapidly in Fraction 9 that the condenser had to be steam-jacketed to carry on further distillation. The specific gravities were determined with a pycnometer, the index of refraction with a Pulfrich refractometer.

From this data the curves in Fig. II were plotted.

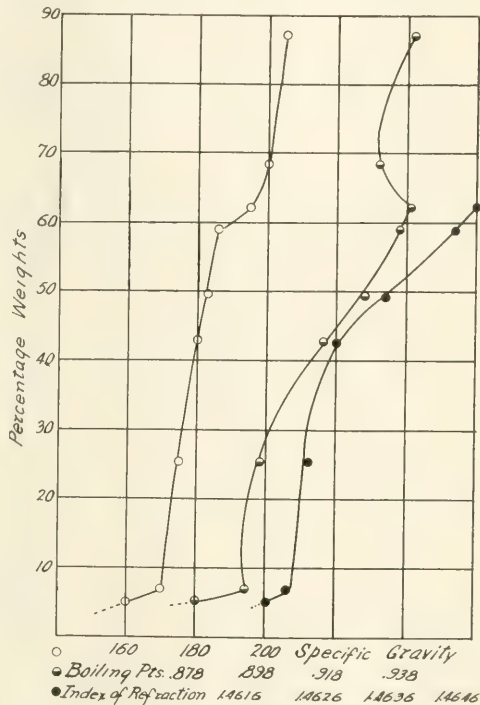


FIG. II—BOILING POINT, SPECIFIC GRAVITY, INDEX OF REFRACTION CURVES FOR SAGE OIL

An examination of the curves in Fig. II shows at least five components with possible traces of others. The first component is largely separated in Fractions 1 and 2; Fractions 3 to 7 contain at least two constituents and Fractions 8 and 9 two more. The sharp breaks between Fractions 2 and 3 and 7 and 8, particularly noticeable in the specific gravity curves, indicate a sharp separation of the constituents at these points.

Fractions 1 and 2 were again redistilled, and with the exception of a small amount of resinous matter, practically all distilled at the boiling point of pinene. This well-cooled, dry oil was saturated with hydrochloric acid and after some time almost completely solidified; after one recrystallization from alcohol the crystals melted at 130° C. Pinene hydrochloride melts at 131° C. The yield of pinene corresponded to somewhat over 6 per cent of the whole material.

Fractions 3 to 7, after redistillation, were first tested

for cineol. To the well-cooled oil, glacial phosphoric acid was slowly added according to Scammel's process.<sup>1</sup> After decanting as much of the oil as possible the magma was placed in a Büchner filter, the filter placed in a centrifuge cup and centrifuged; in this way we were able to get the magma fairly dry without the loss of any of the adhering oil. After decomposition of the phosphate with hot water, a pure oil was obtained, which melted at  $-1^{\circ}\text{C}$ . The cineol thus obtained constituted 30 per cent of the whole. The cineol was also identified by the formation of the iodol which, after recrystallization from benzene, melted at  $111-112^{\circ}$ .

The oil remaining in Fractions 3 to 7 after the removal of the cineol constituted approximately 25 per cent of the whole. This part of the oil was optically inactive and the boiling point and specific gravity indicated either terpinene or dipentene. An attempt was made to form the dipentene tetrabromide, but although crystals separated they were not in sufficient quantity to be identified. On treatment of the oil with Beckmann's reagent<sup>2</sup> (30 parts water, 6 parts potassium dichromate and 5 parts sulfuric acid), a heavy brown precipitate separated which showed that a considerable portion of the oil consisted of terpinene.

Fractions 8, 9 and 10 were subjected to a freezing mixture of ice and hydrochloric acid, a temperature  $-20^{\circ}$  being attained. Solid crystals amounting to 25 per cent of the total oil separated. After the first sublimation these crystals showed slight optical activity, but after the second sublimation were optically inactive. They melted at  $173^{\circ}\text{C}$ . Pure camphor melts at  $175^{\circ}$ . The semicarbazone prepared according to the method of Tiemann,<sup>3</sup> melted at  $232^{\circ}$ . The semicarbazone of camphor melts at  $236-238^{\circ}$ . Undoubtedly these crystals were camphor. After the removal of the camphor there remained approximately 10 to 12 per cent of the original oil. The boiling point was  $200^{\circ}\text{C}$ , specific gravity  $0.917$ , and specific rotation about  $25.9^{\circ}$ . To a solution of the oil in petroleum ether, bromine was slowly added according to the method of Wallach<sup>4</sup> for preparing thujone tribromide; crystals were obtained which, after twice recrystallization from ethyl acetate, melted at  $123-124^{\circ}$ . Thujone tribromide melts at  $122^{\circ}$ .

A small quantity of oily substance remained from Fractions 8, 9 and 10 after the separation of the camphor and thujone; this was a resinous oil, probably partly formed by polymerization during the process of distillation, and partly consisting of other high boiling terpenes which occurred in quantities too small to be definitely determined.

	Analysis by Bureau of Plant Industry	Our analysis
1 Pinene.....	?	6.0 per cent
2 Cineol.....	22.5 per cent	30.0 per cent
3 Dipentene, terpinene, etc.....	?	25.0 per cent
4 Thujone.....	Trace	8.0 per cent
5 Camphor.....	40.0 per cent	25.0 per cent
6 Resinous material.....	?	5.0 per cent

A comparison of our analysis with that of the Bureau

of Plant Industry gives a good indication as to the variation of the constituents of the oil with the season.

At the earlier season at which we obtained our material, the oil contains a considerably higher percentage of the lower boiling constituents, while at the later period a somewhat greater percentage of camphor was found.

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### EXAMINATION OF CHINESE WOOD OIL<sup>1</sup>

By E. E. WARE AND C. L. SCHUMANN

The use of Chinese wood oil as a varnish oil, although of fairly recent adoption, except in the Orient, has increased rapidly until at the present time wood oil has come to be considered the important oil of the varnish industry.

The value of the oil has been said to lie in its ability to form actual combinations with the abietic acid of the rosin with which it is cooked. This statement may be open to question, but the fact remains that varnishes of superior quality can be made from wood oil and rosin when they are properly manipulated.

Most of the Chinese wood oil imported into the United States is gathered in small quantities throughout the rural districts of western China, and after passing through the hands of several native collectors and dealers, reaches Hankow, where it is put into the export packages. The American buyer, although reasonably certain that he receives the oil as packed at Hankow, has no assurance that the oil he buys is representative of the oil as pressed from the nut. The wide variations that the varnish-maker finds in the oil as he uses it may be due to variations in the nut and in its treatment, or to adulteration by one or more of the various middlemen during its open-basket travel from interior China to the forwarder's warehouse at Hankow.

### METHODS OF EXAMINATION

Numerous methods have been proposed for the determination of the relative purity of wood-oil samples. Polymerization of the oil by heating at a definite temperature for a definite length of time, various modifications of which treatment have been proposed by Bacon, Worstall, Potsdamer, Browne, and others,<sup>2</sup> is the method in most general use at the present time. This method seems to have given the most satisfaction, since the analytical constants of wood oil vary within rather wide limits, and this variation does not seem to be accompanied by a corresponding variation in the working qualities of the oil, as judged by its action in the varnish kettle.

However, many buyers prefer to depend upon the analytical constants in passing judgment on wood oil, claiming that the personal equation has too strong an influence on the results obtained by the heat polymerization method. The iodine number and the re-

<sup>1</sup> U. S. Pharm., 1900, p. 313.

<sup>2</sup> Baeyer, *Ber.*, 27, 815.

<sup>3</sup> Tiemann, *Ibid.*, 28, 2191

<sup>4</sup> *Ibid.*, 275, 190, 286, 129

<sup>1</sup> Presented at the 17th Annual Meeting of the American Society for Testing Materials, Atlantic City, June 30 to July 3, 1914.

<sup>2</sup> Boughton, "Testing of Chinese Wood Oil," *Proceedings Am. Soc. Test. Mats.*, 13 (1913), 923.

fractive index<sup>1</sup> seem to be the most reliable constants to use.

McIlhiney<sup>2</sup> offers a method for the examination of this oil that promises well when standardized. He precipitates the insoluble iodine addition products formed when wood oil is treated with iodine in acetic acid solution, and weighs the oil remaining after evaporation of the solvent from the filtrate.

#### LIGHT BREAK

A familiar characteristic that seems to have been neglected in the consideration of methods for judging the purity of wood-oil samples, is the light "break." It is a well-known fact that wood oil exposed to the light in bulk soon exhibits a flocculent white precipitate, which continually increases in amount until, after some months, the oil seems to be a solid white mass. This change in wood oil upon exposure to light is reported by Normann<sup>3</sup> to be a polymerization. Fahrion<sup>4</sup> does not agree with this view but calls the change a molecular transformation. Normann also finds that light has a similar effect upon the potash soap of Chinese wood oil and that the transformation takes place more rapidly than with the oil.

This break caused by sunlight seems to be characteristic of wood oil alone, and seems to be capable of standardization to the point that permits its use as an analytical method for the estimation of the purity of wood-oil samples.

The authors in studying this phenomenon have made use of certain catalytic agents that markedly influence the rate of transformation. Among these are iodine, sulfur,<sup>5</sup> hydriodic acid, sulfur chloride, carbon dioxide, hydrogen sulfide, phosphorus tribromide, and carbon bisulfide.<sup>6</sup> These agents act at different rates, and bring to completion, in times varying from a few hours to several weeks, a reaction that Morrell<sup>7</sup> reports as proceeding only to the extent of 6 per cent in one year. Sulfur chloride and iodine are the only accelerators studied that will cause a complete precipitation within the time that permits the operation to be classed as an analytical method. Others of the catalyzers might be used as a means of getting a less contaminated product for the examination of its characteristics.

The action of sulfur chloride upon the drying and semi-drying oils is common knowledge. Jenkins<sup>8</sup> reports the fact that sulfur chloride added to wood oil to the extent of 20 per cent will yield a jelly-like mass. The reaction is accompanied by an evolution of hydrochloric acid and considerable heat. Chinese wood oil is not alone in exhibiting this characteristic, some of the semi-drying oils showing quite as energetic an action toward sulfur chloride. The fact that such compounds are formed may not therefore be accepted as a test for the purity of wood oil. Gardner<sup>9</sup> suggests

that as Chinese wood oil in carbon tetrachloride solution will form this addition product much more rapidly than will other oils under the same conditions, the action might be susceptible to a time standardization.

If the wood oil be thinned with a solvent upon which the sulfur chloride will not act, and the dilution be to a strength of solution of 20 per cent or less, the sulfur chloride then becomes merely a catalytic agent for the transformation of the wood oil by light, and there seems to be very little if any addition product formed. The oil will break to a considerable extent even in the dark, but the reaction is very much more rapid if exposed to light. If the concentration of the sulfur chloride be low and the mass cool, the reaction will proceed until within a few hours the oil is of the consistency of lard. In order that the reaction proceed to completion it is necessary that the break be filtered out at intervals.

The reaction between Chinese wood oil and iodine has been used as a qualitative,<sup>1</sup> and the modification introduced by McIlhiney as a quantitative method for the estimation of the purity of wood oil. If we carry the thinning still further than is recommended by McIlhiney, and use petroleum ether instead of glacial acetic acid, the addition of 0.3 per cent of iodine will give practically no additional products, but will accelerate the transformation of the oil into the insoluble elaeostearic glyceride of Fahrion.

**ANALYTICAL METHOD NO. 1**—The authors' procedure is as follows: Five grams of the oil to be examined are weighed into a small beaker, thinned with 25 cc. of petroleum ether (60° C. b. p.), and the whole cooled to 0° C. After cooling, 5 cc. of ice-cold, saturated solution of iodine in petroleum ether are added with stirring. Precipitation starts within a few minutes; the better the light the quicker the precipitation. After about 1 hour, more petroleum ether is added and the mass stirred thoroughly. The first filtration should take place after about 3 hours, the precipitation having proceeded by that time to show a conversion of about 50 per cent of the wood oil present. Little is gained by waiting longer before filtering, as the precipitate is so heavy as to mask the further action of light upon the oil. The filtrate from the first filtration is cooled and again exposed to light. A few milligrams of iodine in solution may be added at this point if the solution has become colorless. Three precipitations with the corresponding filtrations are generally sufficient to give total yield. The solution should be kept cold at all times during precipitation, although after each filtration the extra petroleum ether may be evaporated on the steam bath, if the solution be thoroughly cooled before the further addition of iodine and the exposure to light.

The material taken out by the third filtration is of somewhat different character from that precipitated earlier in the operation. This may indicate the presence of a third glyceride as a constituent of wood oil, and may account for the difference of opinion between Cloez,<sup>2</sup> who claims 75 per cent elaeomargaric acid and

<sup>1</sup> Wise, *This Journal*, **4** (1912), 497.

<sup>2</sup> *Ibid.*, **4** (1912), 496.

<sup>3</sup> *Chem. Ztg.*, **31** (1907), 186.

<sup>4</sup> *Chem. Centrbl.*, **83** (1912), 2154.

<sup>5</sup> Maquenne, *Compt. rend.*, **135** (1902), 696.

<sup>6</sup> Andes, "Iron Corrosion and Anti-Corrosive Paints," p. 156.

<sup>7</sup> *Transactions Chem. Soc.*, **101** (1912), 2082.

<sup>8</sup> *J. Soc. Chem. Ind.*, **16** (1897), 195.

<sup>9</sup> *Proceedings Am. Soc. Test. Mats.*, **13** (1913), 946.

<sup>1</sup> Boughton, *J. Soc. Chem. Ind.*, **28** (1909), 719.

<sup>2</sup> *Compt. rend.*, **81** (1875), 469.



25 per cent oleic acid, and Fahrion<sup>1</sup> who finds 90 per cent and 10 per cent.

In Table I are compiled the data obtained by the

TABLE I. EXAMINATION BY PRECIPITATION OF LIGHT BREAK

SAMPLE No. G.	ADULTERANT G.	Kind	Oil precipitated			ADULTERANT		
			Residue %	calculated %	Residue calculated %	Calculated Present %	Found %	
1	5.000		0.365	92.7	0.350	0.015	0.0	0.3
1	5.085		0.415	91.8	0.353	0.062	0.0	1.2
1	5.440	1.010	1.335	94.0	0.381	0.954	15.7	14.8
1	5.160	1.000	1.400	92.2	0.361	1.039	16.2	16.9
1	5.040	0.580	0.920	93.3	0.353	0.567	10.3	10.1
1	5.120	0.500	0.815	93.8	0.358	0.457	8.9	8.2
1	5.030	1.040	1.400	92.8	0.352	1.048	17.2	17.3
1	5.010	1.010	1.350	93.6	0.357	0.973	16.8	16.1
1	5.945	1.665	1.920	94.8	0.346	1.574	25.2	23.8
1	6.680	0.420	0.940	92.2	0.468	0.472	5.9	6.6
1	5.180	0.495	0.825	93.6	0.363	0.462	8.7	8.1
1	5.040	0.280	0.650	93.1	0.353	0.297	5.3	5.6
1	5.810	1.150	1.470	95.3	0.477	0.993	14.5	12.5
2	5.130		0.320	93.6	0.359	-0.039	0.0	-0.6
2	5.135		0.360	93.0	0.360	0.000	0.0	0.0
3	5.135		0.300	94.1	0.360	-0.060	0.0	-1.1
3	5.600		0.360	93.6	0.392	-1.032	25.0	-0.6

NOTE.—Wood oil No. 1 was furnished by the Acme White Lead and Color Works, and is a Hankow oil of high quality. Wood oils Nos. 2 and 3 are the standard oils from the American Society for Testing Materials, and were furnished through the courtesy of Mr. H. A. Gardner and Mr. L. P. Nemzek.

use of this method in the examination of several Chinese wood oils and of other samples in which these oils were mixed with varying amounts of sesame and soya bean oil. The figures in the column entitled "Adulterant (calculated)" were obtained as the difference between the actual weight of the residue and the calculated weight, using 7 per cent of the weight of the wood oil in the sample as the average weight of residue obtained from pure oil. In cases where the figures show negative, indicating an actual weight less than the calculated, the figures were inserted merely to show the extent to which the inaccuracy of the method is apparent.

The results in Table I indicate a precipitation of approximately 93 per cent of the wood oil present, when using iodine as a catalyzer. Sulfur chloride does not seem to be so efficient in its action upon the raw oils. The precipitation proceeds at a slower rate, and there seems to be a strong tendency for the material to skin over with an oxidized film during the precipitation. No quantitative results on sulfur chloride precipitation are included in the table.

The method of estimation used in arriving at the figures given in Table I is the weighing of the final filtrate after evaporation of the petroleum ether. The amount of adulteration may be considered as the weight of the filtrate minus the amount of the residue due to the unprecipitated olein present in the wood oil. This amount of unprecipitable matter has been taken as 7 per cent of the wood oil, that amount having been shown to be an average for a number of determinations on supposedly pure wood oil.

It is possible to get an estimation of the amount of wood oil present by the direct weighing of the precipitated matter. In that case great care must be exercised to prevent oxidation of this material during drying.

The tabulated results show the possibilities of this method as a means of detecting adulteration in wood oil. It is certain that further refinement of the method is possible, which will add to its accuracy.

# INSOLUBLE SOAP

In studying the characteristics of this solid precipitated glyceride, it was noted that the potassium soap was but slightly soluble in absolute alcohol, which agrees with the findings of Normann<sup>1</sup> and Morrell<sup>2</sup> who worked on the material precipitated by sunlight alone. Morrell, however, also states that the soap is practically insoluble in water, which statement is not borne out by the experience of the authors.

The comparative insolubility of the potassium soap of Chinese wood oil offers possibilities of a rapid method for the detection of adulteration in wood-oil samples. The saponified product separates quite completely from absolute alcoholic potash, and may be washed free from the soap of the adulterating material. If the method be carried out at uniform temperature, preferably 0° C., and the alcohol for washing the precipitate be previously saturated with the soap, it is possible to estimate the amount of adulteration within fairly narrow limits.

ANALYTICAL METHOD NO. 2.—A 3-g. sample of the oil to be examined is saponified with 100 cc. of *N*/4 absolute alcoholic potash for one-half hour, using an air condenser of sufficient length to prevent the loss of alcohol. The saponified mixture is cooled to 0° C., held for 10 minutes at that temperature, and filtered through a Gooch crucible using a filter-paper disk instead of an asbestos pad. The precipitate, after washing thoroughly with ice-cold saturated absolute alcohol, is removed from the crucible to a cover glass, and is dried at 75 to 80° C., under vacuum, and with a stream of dry hydrogen or carbon dioxide passing through the desiccator. After cooling without removing from the desiccator, the precipitate is taken out and weighed, and the weight calculated to wood oil.

It is necessary, if the method is to be at all accurate, to use absolute alcohol both for saponification and for washing the precipitate, as the soap is appreciably soluble in the presence of even small amounts of water. This alcohol and alcoholic potash should be freshly saturated with the soap before use, for although the soap is but slightly soluble in absolute alcohol, that solubility changes on standing, especially if exposed to light. It is a comparatively easy matter to keep freshly saturated solutions ready for use by making up a batch of the soap and introducing it into the stock bottles of alcohol and alcoholic potash, in quantities more than sufficient to saturate them at 0° C. When about to make a determination, the solution may be warmed until an appreciable amount of soap goes into solution, after which it may be cooled to 0° C. and held for 10 minutes and filtered. This fresh filtrate is ready for use, and the fact that the procedure followed will be duplicated on the saponified sample helps to insure the accuracy of the determination.

During the washing of the precipitate the whole must be kept cold, for the solubility of the material in alcohol is greatly increased by a rise in temperature. This is accomplished by filtering through a Gooch crucible surrounded by cracked ice. The authors

<sup>1</sup> Chem. Ztg., **31** (1907), 188.

<sup>2</sup> Trans. Chem. Soc., **101** (1912), 2082.

<sup>1</sup> Chem. Centrbl., **83** (1912), 2154.

have found the apparatus shown in Fig. 1 to be quite satisfactory.

The precipitate is susceptible to oxidation and must be kept away from air during drying. Also, the fact that high temperature will char the soap limits the drying temperature to about 80° C. The precipitate may be dried in a desiccator connected by a long rubber tubing to a source of hydrogen or carbon dioxide, and to a vacuum pump. After introducing the precipitate to be dried, the desiccator may be placed in a low-temperature steam drying oven for 3 hours.

The results obtained by the use of the insoluble-soap method and the data from which these results were computed, are compiled in Table II. In calculating the results for this table it was decided to accept the weight of the dried insoluble soap as representative of the weight of wood oil present in the sample, since the error of this assumption was considered to be within the limits of error of the method.

Although neither of the above methods has proved entirely satisfactory as a method for the estimation of wood oil in rosin varnishes, the efforts made to apply them to that end have resulted in some interesting data regarding the conditions existing in this type of varnish.

TABLE II—EXAMINATION BY PRECIPITATION OF INSOLUBLE POTASSIUM SOAP

SAMPLE No.	G.	ADULTERANT G.	Kind	Soap G.	Calculated %	Recovered %	ADULTERANT Found		
							G.	%	Present %
1	3.301			3.334	3.334	101.0	-0.033	1.0	
1	2.814	0.304		2.807	2.807	99.8	0.311	9.9	9.8
1	3.012	0.180	Linseed	3.021	3.021	100.3	0.171	5.5	5.6
1	2.516	0.506		2.508	2.508	99.8	0.514	17.0	16.7
1	3.138			3.170	3.170	101.0	-0.032	1.0	
1	2.859	0.591	Soya	2.874	2.874	100.6	0.944	24.7	23.8
1	2.642	0.881	bean	2.645	2.645	100.1	0.878	24.9	25.0
1	3.013			3.006	3.006	99.8	0.007	0.2	
1	3.006	0.167	Soya	2.982	2.982	99.2	0.191	6.0	5.3
1	2.051	1.302	bean	2.020	2.020	98.1	1.333	39.8	38.9
1	2.461	0.125		2.536	2.536	103.0	-0.075	2.9	4.8
1	2.791	0.607		2.883	2.883	103.3	0.515	15.2	17.9
1	2.742	0.380	Linseed	2.761	2.761	100.7	0.361	11.5	12.2
1	2.742	0.183		2.741	2.741	100.0	0.184	6.3	6.3
1	2.528			2.501	2.501	98.9	0.027	1.1	
1	2.524			2.550	2.550	101.0	-0.026	-1.0	
1	2.521			2.510	2.510	99.5	0.011	0.5	
1	2.510			2.514	2.514	100.2	-0.004	-0.2	
1	2.321	0.707		2.367	2.367	102.0	0.661	21.8	22.4
1	2.428	0.738	Linseed	2.508	2.508	103.3	0.658	20.8	23.3
1	3.019			3.019	3.019	100.0			
1	3.039	0.409		3.025	3.025	99.5	0.423	12.3	11.9
1	3.199	0.049	Mixed	3.201	3.201	100.3	1.038	24.5	24.7
2	3.252			3.224	3.224	99.1	0.028	0.9	
3	3.471			3.544	3.544	102.1	-0.073	-2.1	
4	3.156			3.014	3.014	95.5	0.142	4.5	
4	3.190			3.092	3.092	96.9	0.098	3.1	

NOTE:—Wood oils Nos. 1, 2 and 3 were the same as those in Table I. Wood oil No. 4 was furnished by Mr. L. P. Nemzek, representing the Educational Bureau of the Paint Manufacturers' Association. This oil is from American-grown nuts.

An examination of the separated constituents of a Chinese-wood-oil rosin varnish seems to show that the polymerization of wood oil in the presence of rosin is practically as complete as in the oil, subject to the same heat treatment in the absence of rosin. The fatty acid in each case shows a molecular weight double that of the fatty acid of raw wood oil. The difference in characteristics between these two polymerized products has not as yet been satisfactorily accounted for.

A comparison of the molecular weights of the fatty acids from raw wood oil and the light breaks seems to show that this light break is an isomer rather than a polymer, and that there is practically no difference between the light break formed slowly by sunlight alone and that catalyzed by iodine.

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## OILS OF THE CONIFERAE. II—THE LEAF AND TWIG, AND BARK OILS OF WHITE FIR

By A. W. SCHORGER

Received August 15, 1914

The white fir [*Abies concolor* (Gord.) Parry] is found on the mountain slopes from southern Oregon to Lower California and from Nevada, Utah, and southern Colorado through Arizona and New Mexico. The dense crown consists of short, heavily foliated branches. The leaves at the top of the tree are usually 1 to 1 1/4 inches in length, while those of the lower branches are somewhat longer—1 1/4 to 3 inches.

### LEAF AND TWIG OILS

The oils were greenish yellow in color with a green fluorescence with the exception of samples Nos. 2439 and 2487, which were lemon-yellow in color and showed no fluorescence. The residue left after removal of the terpenes by distillation was fluorescent to a marked degree, but this property was not noted in the "green oil" fraction obtained, though the oil owes its green color to this fraction.

The properties of the oils and the yields are given in Table I.

TABLE I—PROPERTIES OF OILS

Sample No.	$d_{40}^{20}$	$n_{D, 20}^{20}$	$\alpha_{D, 20}^{20}$	Ester					Per cent alcohol		Yield of oil Per cent
				Acid No	Ester No	No after acetyl-ation	Ace-tate Per cent	Free	Total		
LEAF AND TWIG OILS											
2176	0.8758	1.4788	-27.94	1.13	12.52	48.88	4.38	10.28	13.73	0.140	
2180	0.8738	1.4786	-20.18	1.81	27.34	54.58	9.57	7.65	15.17	0.029	
2181	0.8732	1.4786	-21.65	1.43	24.03	52.45	8.41	7.99	14.60	0.050	
2183	0.8737	1.4796	-26.87	1.07	20.55	54.22	7.19	9.50	15.15	0.150	
2439	0.8720	1.4787	-26.59	1.01	14.48	51.83	5.07	10.57	14.55	0.163	
2440	0.8745	1.4790	-24.08	1.32	14.80	47.84	5.18	9.32	13.39	0.095	
2487	0.8777	1.4781	-20.11	1.06	18.79	55.51	6.58	10.39	15.56	0.272	
							Mean, 6.63	9.39	14.59	0.128	
BARK OILS											
			$\alpha_{D, 20}^{20}$								
2209	0.8767	1.4833	-20.95	1.22	6.88	23.34	2.41	4.58	6.48	0.07	
2423	0.8702	1.4809	-20.15	0.87	6.43	20.45	2.25	3.90	5.67	0.12	
							Mean, 2.33	4.24	6.08	0.095	

There is a considerable variation in the ester and free alcohol content in the various samples but the total alcohol content is fairly uniform. Samples Nos. 2439 and 2440 were distilled from material taken from the top and base, respectively, of the same tree. The needles from the top of the tree show a slightly greater total alcohol content.

Six hundred grams of oil distilled as follows: 161-165°, 15.5 per cent; 165-170°, 42 per cent; 170-180°, 18.5 per cent; 180-195°, 3 per cent; 195-240°, 13 per cent; 240-310°, 3 per cent.

### IDENTIFICATION OF CONSTITUENTS

FURFURAL—The first fraction was shaken out with water. On treating the aqueous extract with aniline and hydrochloric acid a deep crimson color characteristic of furfural was obtained.

$\alpha$ -PINENE—The fraction examined for  $\alpha$ -pinene had

the following properties: B. p.  $156.5^{\circ}$ – $150.0^{\circ}$ ,  $d_{15}^{\circ}$  0.8671,  $\alpha_{D_{20}}^{\circ}$   $-24.29^{\circ}$ . The nitrosochloride separated very slowly from the mother liquor. The purified compound melted at  $103^{\circ}$  and its nitropiperidine at  $118.5^{\circ}$ . The total fractions boiling below  $160^{\circ}$  amounted to 75 g. (12.5 per cent).

**CAMPENE**—The camphene fraction b. p.  $160$ – $164^{\circ}$  amounted to 8 per cent. The fraction b. p.  $160$ – $162^{\circ}$ ,  $d_{15}^{\circ}$  0.8695,  $\alpha_{D_{20}}^{\circ}$   $-27.39^{\circ}$ , was tested according to the method of Betram and Walbaum.<sup>1</sup> On treating the saponified product with water the isoborneol separated as a viscous oil. On steam distillation oil first passed over, followed by isoborneol that solidified in the condenser. The purified isoborneol melted at  $209$ – $210^{\circ}$  in a sealed tube. The fraction b. p.  $162$ – $164^{\circ}$  yielded smaller amounts of isoborneol.

**$\beta$ -PINENE**—This terpene is the major constituent of the leaf oil, since 254 g. (42.3 per cent) were finally obtained boiling between  $164$ – $170^{\circ}$ . On oxidation of a fraction, b. p.  $164$ – $166.5^{\circ}$ ,  $d_{15}^{\circ}$  0.8715,  $\alpha_{D_{20}}^{\circ}$   $-23.66^{\circ}$ , with alkaline potassium permanganate, large quantities of sodium nopinote were obtained. The free nopinic acid melted at  $126.6$ – $127^{\circ}$ .

**PHELLANDRENE**—The fractions b. p.  $170$ – $180^{\circ}$ , weighing 90 g., gave large amounts of phellandrene nitrite. The fraction b. p.  $174$ – $177^{\circ}$ ,  $d_{15}^{\circ}$  0.8572,  $\alpha_{D_{20}}^{\circ}$   $-28.74^{\circ}$ , formed a solid mass of crystals on treatment with  $KNO_3$  and acetic acid. The nitrite melted at  $102^{\circ}$ . Limonene was not detected as either the dihydrochloride or tetrabromide.

**BORNEOL**—The oil obtained by saponification of the fraction b. p.  $200$ – $240^{\circ}$  distilled in about equal proportions between  $205$ – $215^{\circ}$  and  $215$ – $220^{\circ}$ . The first portion had the rotation  $\alpha_{D_{24}}^{\circ}$   $-29.16^{\circ}$ . Both fractions were treated with phthalic anhydride. Saponification of the phthalic esters yielded oils. On oxidizing the latter with chromic acid mixture camphor was obtained melting at  $171$ – $172^{\circ}$ . Considerably larger yields of camphor were obtained by oxidizing the borneol fraction directly with saturated potassium permanganate solution without attempting its purification through the phthalic ester. The camphor was converted to its semicarbazone melting at  $236$ – $237^{\circ}$ .

**ACETIC ACID**—The acids recovered from the ester saponification liquors were precipitated as their silver salts in five fractions. Analysis of portions of the various precipitates without further purification gave a silver content of 63.04, 63.72 per cent, showing that acetic acid must be practically the only acid present, since silver propionate theoretically requires 59.91 per cent Ag, silver acetate 64.64 per cent Ag, and silver formate 70.59 per cent Ag. The combined precipitates were recrystallized from water several times. The fine needles obtained were analyzed as follows:

0.1140 g. silver salt gave 0.0736 g. Ag = 64.56 per cent Ag.

**"GREEN OIL"**—The residue remaining after removal of the ester fraction had a strong green fluorescence. The fraction b. p.  $240$ – $310^{\circ}$  on redistillation distilled mainly between  $265$ – $285^{\circ}$ . It had  $d_{15}^{\circ}$  0.925,  $n_{D_{15}}^{\circ}$  1.4936,  $\alpha_{D_{20}}^{\circ}$   $-0.49^{\circ}$ , for a 37.83 per cent solution

in ether. The oil was emerald-green in color and showed no fluorescence. No solid derivatives were obtained. This oil appears to be similar to the "green oil" obtained by the author from the leaf oil of Douglas fir<sup>1</sup> and showed the same color reactions.

#### BARK OIL

The bark distilled was about one-quarter of an inch thick and had been peeled from small trees cut for poles. The properties of the oils and the yields are given in Table I.

The following results were obtained on distillation of 110 g. of oil: b. p.  $162.5$ – $170^{\circ}$ , 65 per cent; b. p.  $170$ – $180^{\circ}$ , 14 per cent; b. p.  $180$ – $192^{\circ}$ , 8 per cent;  $192$ – $250^{\circ}$ , 4 per cent;  $250$ – $300^{\circ}$ , 5 per cent.

#### IDENTIFICATION OF CONSTITUENTS

**FURFURAL**—This aldehyde was detected in the first fraction by the color method. From the intensity of color produced a larger quantity of furfural is present in the bark oil than in the leaf and twig oil.

**$\alpha$ -PINENE**—By repeated fractionation 10 g. (9.1 per cent) of oil were obtained of b. p.  $160$ – $163^{\circ}$ ,  $\alpha_{D_{20}}^{\circ}$   $-16.43^{\circ}$ . This oil yielded 2.1 g. (21 per cent) of pinene nitrosochloride. Its nitropiperidine melted at  $118^{\circ}$ .

**$\beta$ -PINENE**—The  $\beta$ -pinene fractions distilled as follows: (1) b. p.  $163$ – $165^{\circ}$ , 14.9 g.; (2) b. p.  $165$ – $170^{\circ}$ , 51.2 g. The latter fraction had  $d_{15}^{\circ}$  0.8654,  $\alpha_{D_{20}}^{\circ}$   $-22.52^{\circ}$ . On oxidation of the oil a yield of 21.7 per cent of sodium nopinote was obtained. The free nopinic acid melted at  $126$ – $127^{\circ}$ . Five grams of sodium nopinote yielded 24 per cent of nopinone, whose semicarbazone melted at  $188^{\circ}$ .

**DIPENTENE**—The oil boiling between  $170$ – $180^{\circ}$  had the rotation  $\alpha_{D_{21}}^{\circ}$   $-29.37^{\circ}$ . On treating the dry oil with dry HCl gas a dihydrochloride m. p.  $49$ – $50^{\circ}$  was obtained, but no solid derivative was obtained on bromination.

**ALCOHOL FRACTION**—The amount of oil obtained by saponification of the fraction b. p.  $192$ – $250^{\circ}$  was too small for identification of the alcohol present. The ester and free alcohol have been calculated as bornyl acetate and borneol as it is most probable that these are the constituents present.

**"GREEN OIL"**—The fraction b. p.  $250$ – $300^{\circ}$ , weighing 5.4 g., was bright green in color and from its color reactions appeared identical with the "green oil" from the leaf and twig oil. It is possible that the "green oil" in the leaf and twig oil is not derived from the needles themselves, but from the bark of the twigs.

#### SUMMARY

The oils of white fir have approximately the following composition:

Percentages	Leaf and Twig oil	Bark oil
Furfural	Trace	Trace
<i>l</i> - $\alpha$ -Pinene.....	12	9
<i>l</i> -Camphene.....	8	
<i>l</i> - $\beta$ -Pinene.....	42	60
<i>l</i> -Phellandrene.....	15	12 13
Ester as bornyl acetate	0.5	2.6
Free borneol.....	9.5	4.5
"Green oil".....	3	5
Losses.....	4	7

FOREST PRODUCTS LABORATORY  
FOREST SERVICE, U. S. DEPARTMENT OF AGRICULTURE  
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<sup>1</sup> *Jour. fur prakt. Chem.*, [2] **49** (1894), 1.



# A NEW METHOD FOR THE DETERMINATION OF ZINC IN TREATED WOOD

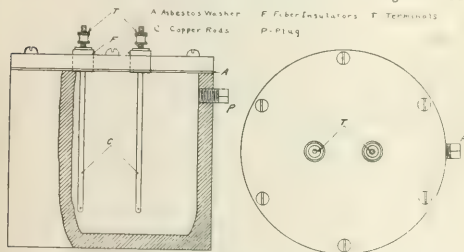
By M. HUME BEDFORD AND R. PFANSTIEL

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Several methods have been proposed for the determination of zinc in wood treated with zinc chloride. Each of these methods is based upon the manner in which the organic matter is destroyed. In the case of hard woods, particularly red oak, it was found that certain organic compounds were not destroyed by some of the ordinary processes, and called for a modified and prolonged operation. For this reason this investigation has been confined to treated red oak.

Francis C. Frary<sup>1</sup> and M. Gordon Mastin use a nickel crucible and fuse the wood shavings with potassium hydroxide and a small quantity of potassium nitrate, added to complete the oxidation of the organic matter. In the above article, mention is made of a method by L. A. Stenger, in which the sawdust is digested with dilute sodium hydroxide solution. The zinc is then determined by electrolysis. Ernst Bateman<sup>2</sup> describes a modified Kjeldahl digestion for destroying the organic matter. In this method the wood shavings are heated with a mixture of nitric acid and potassium chlorate and finally sulfuric acid is added and the excess of nitric acid is evaporated off.

In the method here proposed the wood is burned in an iron bomb with sodium peroxide. The accompanying figure shows the design of the bomb. The bowl is about 4 1/2 in. internal diameter and 5 in. deep,



with walls 3/8 in. thick. The plug *P* is taken out after firing a charge for the purpose of injecting water. This prevents any loss from foaming which takes place when water is added.

Several methods of determining the zinc after the wood had been burned were tried, but the one that gave the best results is practically the same as the one used by Bateman. The details of the procedure as finally adopted are as follows: 3 grams of red oak sawdust, previously dried at 110° C., are treated with 1 cc. of zinc chloride solution equivalent to 0.0350 g. of metallic zinc and dried at 110° C. The sawdust is then mixed with 35 g. of sodium peroxide and fired in the bomb. After the explosion the bomb is cooled in water, and distilled water added through the plug *P*. The contents are dissolved by heating on a water bath. The solution is then transferred to a beaker, acidified with concentrated hydrochloric

acid and boiled for a few minutes. Two grams of citric acid, 10 cc. concentrated nitric acid, and 5 cc. of 8 per cent ferric chloride solution are added. The solution is then made alkaline and 2 cc. excess of concentrated ammonium hydroxide are added. After dilution to 400 cc., the solution is titrated at 80° C. with potassium ferrocyanide. An outside indicator of equal parts of glacial acetic acid and glycerine is used.

The potassium ferrocyanide solution is made by dissolving 5 grams of the salt in one liter of water and is standardized against the zinc chloride solution under the same conditions as exist in the charge. A blank is also run on 3 grams of the untreated wood and subtracted from each determination.

It is necessary to keep the conditions the same throughout the titration. An excess of ammonia is necessary to keep the solution from turning blue, but a large excess prolongs the end point.

The time required for a determination is about 25 minutes. The accuracy of this method is shown by a set of six consecutive determinations.

## RESULTS

1 Cc. Zinc Chloride Solution (Equivalent to 0.0350 g. Metallic Zinc) Added to 3 Grams of Wood.

No.	ZINC FOUND		ERROR	
	Grams	Per cent of wood	Grams	Per cent of wood
1.....	0.0346	1.153	-0.0004	-0.014
2.....	0.0344	1.147	-0.0006	-0.020
3.....	0.0351	1.170	+0.0001	+0.003
4.....	0.0351	1.170	+0.0001	+0.003
5.....	0.0350	1.167	0.0000	0.000
6.....	0.0348	1.160	-0.0002	-0.007
Average.	0.0348	1.161	-0.0002	-0.005

This method should give as satisfactory results with any other kind of wood as it does with red oak. The simplicity, rapidity, and accuracy of the method should make it useful in industrial laboratories.

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## A NEW QUALITATIVE TEST FOR SILICATES IN SOAP

By HAROLD W. LEITCH

Received June 9, 1914

Silicate of soda, or water glass, is a filler found in many textile, household, and other soaps. Although it may not be harmful in all cases, it is not a desirable constituent of a soap, especially one used in the textile mill. Upon some fibers, and many dyes, its action is decidedly injurious.

The writer has a new qualitative test for soluble silicate in soap, and finds that it works with complete satisfaction in all cases tried.

The principle of the test is the insolubility of aluminum silicate in acetone and water. Briefly, the test is carried out as follows: The soap is dissolved in water, acidified with hydrochloric acid to decompose the soap, and filtered to separate fatty and other insoluble matter. The filtrate is neutralized with alkali, and boiled with alcoholic potash to saponify any oil coming through the paper, as well as to coagulate any gelatin which may be present. It is then filtered to remove the latter, and poured into acetone containing a little water, sodium aluminate and chloride to precipitate the silicate.

<sup>1</sup> THIS JOURNAL, 5, 738.

<sup>2</sup> *Ibid.*, 6, 16.

A number of different soaps of known composition, as well as various mixtures of soap, impurities, and fillers were experimented with and tested. It was found that a satisfactory test could be obtained by using 0.25 g. of soap, containing water glass equivalent to 0.00045 g. (0.18 per cent) of  $\text{SiO}_2$ . To determine what substances would interfere in the test, 40 per cent (based on the actual weight of soap) of sodium carbonate, 40 per cent of potassium carbonate, 20 per cent of borax, 40 per cent of aluminate of soda, 10 per cent of sodium chloride, 10 per cent of sodium sulfate, 20 per cent of dextrin, 20 per cent of corn-starch, 20 per cent of soluble potato starch, 20 per cent of gelatin, 20 per cent of "Diastafor," 20 per cent of glucose, and 20 per cent of sugar were added to separate portions of the pure soap solution, and each of these tested both with and without silicate. Then all possible combinations of two, three and four solutions were tried out. Furthermore, soaps made from the following stocks were tested with and without silicate: tallow, palm oil, linseed oil, red oil, coconut oil, cottonseed oil, and rosin oil. After these numerous unfailling tests it was considered advisable to recommend the procedure given below.

#### PROCEDURE

Dissolve about 1 g. of the sample of soap in 25 cc. of water, and add normal hydrochloric acid 5 cc. in excess of the amount necessary to neutralize the total alkali, using methyl orange indicator. Heat on the water bath until the fatty acids float to the top and the liquid beneath is clear. Filter through ordinary filter paper, make the filtrate neutral or slightly alkaline with normal caustic soda, add 10 cc. of this solution corresponding to about 0.3 g. of the original sample, to 5 cc. of normal alcoholic caustic potash, and boil down to 10 cc. on the steam bath. Pour this clear or filtered solution into a test tube containing 10 cc. of acetone and 1 cc. of a solution made by dissolving 10 g. of pure sodium aluminate and 2 g. of sodium chloride in a liter of water. If water glass is present in the sample of soap, a flocculent gelatinous precipitate results. Dextrin or starch, if present in the soap, will also precipitate here, so that if a test made by adding a drop of iodine solution to a portion of the filtrate from the acidified soap solution shows a blue or reddish brown coloration, a change in the procedure must be made just before the boiling with alcoholic potash. If dextrin or starch is found at this point, add to the neutral or slightly alkaline filtrate about 2 g. of "Diastafor," allow to stand half an hour at a temperature of about 35° C., and then proceed as before.

#### NOTES

If a water solution of a soap containing water glass, gelatin, starch, dextrin, or free oil (of some kinds) is added to the final test solution a precipitate is formed. Whereas a solution of soap having sodium or potassium carbonate, borax, free caustic, sodium sulfate, sodium chloride, sugar, glucose, or "Diastafor" (and provided it has no water glass, gelatin, starch, dextrin, or free oil), if poured into the acetone-aluminate-salt solution produces no precipitate.

The first procedure takes care of matter insoluble

in water or dilute acid (fatty matter, sand, pumice, oat-meal, sawdust, bran, etc.) and gelatin, while the treatment with "Diastafor" rids the solution of dextrin and starch. A special and well known method for separating and identifying gelatin is to treat the soap solution with formaldehyde and evaporate to dryness, when formo-gelatin, insoluble in boiling water, is formed. Thus the soap may be redissolved, the gelatin separated by filtration through fine wire gauze, and the filtrate tested for silicate by the regular method. It is well to make this separation if it is expected that much gelatin is in the soap.

From the above statements it can be seen that it is not always necessary to acidify and filter the soap solution, neither is it always required to boil with alcoholic potash; for, if a soap when dissolved in water and added to the acetone test solution does not give a precipitate, it at once proves that there is no silicate in the sample. However, if a precipitate forms it does not show conclusively that silicate is present, but indicates the necessity of separating the fatty matter, or boiling with alcoholic potash, or both, before making the final test.

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### OXIDATION OF SULFUR COMPOUNDS OF COAL, AND OF NITROGEN IN THE BOMB CALORIMETER, AND THE CORRECTION TO BE APPLIED IN DETERMINING THE HEATING VALUE OF COAL<sup>1</sup>

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#### INTRODUCTION

The chief factor in determining the value of a coal is the heat it evolves by combustion. Extensive investigations made by the United States Geological Survey and by the Bureau of Mines have resulted in a much wider adoption of the heating value of coal as a basis for its purchase. This value is obtained by burning the fuel in a bomb calorimeter under standard conditions such as are described in Technical Paper No. 8 of the Bureau of Mines.

Coal carries sulfur, which by combustion develops heat. It burns in the air to sulfur dioxide ( $\text{SO}_2$ ) but it is claimed that in the calorimeter it burns to sulfur trioxide ( $\text{SO}_3$ ), evolving more heat, and that therefore a correction should be applied to the calorific value obtained in the bomb in order to ascertain the heating value of the coal under ordinary conditions. On the assumption of complete oxidation of the sulfur to sulfur trioxide, the correction applied to the heat value obtained in the calorimeter is 2200 calories per gram sulfur.<sup>2</sup> This correction on a coal containing 2.5 per cent sulfur and valued at \$2.75 per ton amounts to 2 cents per ton.

From what is known of the equilibrium of sulfur dioxide, oxygen, and sulfur trioxide discussed later in this paper, it does not seem probable that the sulfur of coal would burn completely to sulfur trioxide in

<sup>1</sup> This paper was prepared as a dissertation for the degree of Doctor of Philosophy at the University of Michigan. The author completed the thesis but died May 31, 1914, before receiving the degree.

<sup>2</sup> Technical Paper No. 8, Bureau of Mines, p. 15.

the bomb calorimeter unless some catalytic or oxidizing agent were present. A correct knowledge of the products formed in the bomb by combustion of the sulfur is of importance from two viewpoints. It has a financial importance connected with the correction to be made for the sulfur of a coal in obtaining the true heating value. It has an analytical importance as a method of estimating the sulfur content of a fuel by combustion in a calorimeter in excess of oxygen under pressure, and subsequent precipitation of the sulfate from the bomb washings.

The investigations described in the following pages were made in order to determine whether or not the sulfur compounds of coal burn completely to sulfur trioxide in the bomb calorimeter, and if so, what conditions are responsible for complete conversion from the dioxide. In connection with the experiments, a number of heat values were calculated in order to obtain the approximate heating value of pyrites per gram sulfur, and the results are discussed at the close of this paper.

Studies of the effect of pressure upon the production of sulfur trioxide from the combustion of sulfur with excess of oxygen have been made by Walther Hempel<sup>1</sup> and H. Giran.<sup>2</sup>

In Hempel's experiments the combustion of the sulfur was carried out in dry oxygen in small iron containers. One of the products formed by the combustion was determined directly and the other was found by calculation. His results were as follows:

S Gram	Pressure Atmospheres	Percentage S as	
		SO <sub>2</sub>	SO <sub>3</sub>
0.238	31	66.8	33.2
0.268	45	34.7	65.3
0.336	72.5	54.5	45.5

Giran burned the sulfur in a bomb calorimeter in an atmosphere of oxygen and obtained results as follows:

Pressure atmospheres	Percentage original S burned to SO <sub>3</sub>
20	21.9
25	22.8
30	27.2
35	39.4
40	30.7
45	31.2

In the quoted results neither Hempel nor Giran has stated the volume of the bomb or the purity of the oxygen used.

Dr. R. Knietsch, in his discussion of the influence of pressure in the "contact process" for the manufacture of sulfuric acid, has given us some data as to the equilibria of sulfur dioxide, oxygen, and sulfur trioxide.<sup>3</sup> He used platinized asbestos as a catalyst, and the experiments conducted at different pressures show a slight change in percentage conversion of sulfur dioxide to sulfur trioxide with change of pressure, the results being as follows:

Furnace gas at		Percentage			Percentage conversion SO <sub>2</sub> to SO <sub>3</sub>
° C.	Pressure	SO <sub>2</sub>	N <sub>2</sub>	O <sub>2</sub>	
430	Normal	7.21	82.35	10.44	98.90
430	5.3 Atm.	7.21	82.35	10.44	99.49
490	Normal	6.60	82.10	11.30	93.76
490	0.31 Atm.	6.60	82.10	11.30	90.85

<sup>1</sup> *Furnische Berichte*, **23** (1890), 1485.

<sup>2</sup> *Compt. rend.*, **139** (1904), 1219-1221.

<sup>3</sup> "Fifth International Congress of Applied Chemistry," Berlin, 1900, Vol. 1, p. 617.

It is known that the formation of SO<sub>3</sub> at high temperatures is considerably reduced by its dissociation into SO<sub>2</sub> + O<sub>2</sub>, which begins at about 400° C., so that the equilibrium of sulfur SO<sub>2</sub>, O<sub>2</sub> and SO<sub>3</sub> calls for all sulfur as the trioxide at ordinary temperatures. In the combustion of sulfur compounds in excess of oxygen, the SO<sub>2</sub> formed unites very slowly with the oxygen to form SO<sub>3</sub> as the temperature drops. However, the presence of a catalyzer hastens the reaction and at 450° C., in the presence of finely divided platinum, the SO<sub>2</sub> and oxygen rapidly form SO<sub>3</sub> until equilibrium is reached. At higher temperatures the conversion to SO<sub>3</sub> is less complete and at 900° C., practically none of the trioxide is obtained. At any given temperature the yield of SO<sub>3</sub> will be the greater the higher the partial pressure of the oxygen. Theoretically, increase of pressure would tend to increase slightly the proportionate amount of SO<sub>3</sub> formed, as action would tend to go in that direction which would bring about decrease of pressure in the system. The results previously quoted confirm this theory but, although the combustion of coal in the calorimeter is carried out usually at 18 to 30 atmospheres pressure, the foregoing results do not indicate that pressure alone can account for complete conversion of the sulfur content of a fuel to SO<sub>3</sub> in the bomb calorimeter. If the sulfur of coal burns completely to SO<sub>3</sub> as is claimed, there must be factors other than pressure to account for it, and it is our problem to ascertain what catalytic or oxidizing agent produces the effect.

#### RELATIVE AMOUNTS OF THE SULFUR OXIDES FORMED WHEN PYRITES IS BURNED IN THE BOMB CALORIMETER

It is known that in most coals pyrites is the chief source of sulfur although this element may occur in the fuel free or as a constituent part of organic compounds. The equilibrium of SO<sub>2</sub>, O<sub>2</sub> and SO<sub>3</sub>, is, however, independent of the source of the sulfur. It seemed advisable to make a study of the products obtained by combustion of pyrites in a calorimeter, not only because sulfur was wanted in a definite form, but also to ascertain whether or not the ferric oxide formed acted as a catalyzer in conversion of SO<sub>2</sub> to SO<sub>3</sub>, and so a series of experiments were made, varying certain factors which, it was thought, might influence the percentage of sulfur oxidized to the trioxide.

The pyrites was mixed with a combustible of known composition, benzoic acid, obtained from the U. S. Bureau of Standards, and from 0.8 to 1.2 grams of the mixture were used for each combustion. The fuel was briquetted for all experiments, as trial combustions with the loose mixtures gave unsatisfactory results due to spattering of the material. The determinations were made in a gold-lined Atwater bomb of 350 cc. capacity, manipulated approximately as described in the *Journal of the American Chemical Society*, July, 1903. The gases of combustion were conducted from the bomb through an absorption train consisting of: (1) an acid solution of barium chloride to detect the presence of any SO<sub>3</sub> escaping from the bomb; (2) an alkaline solution of bromine water to oxidize any SO<sub>2</sub>



to  $\text{SO}_3$ . A Friedrich washer which was used for the bromine solution proved very efficient, no sulfur dioxide being detected at the end of the train where tests were made.

When the bomb was emptied of gases it was rinsed out seven times with water free from acid, the washings were heated to expel any  $\text{SO}_2$  that might be present in solution, cooled, and then titrated for total acidity. After titration, the sulfate contained in the washings was precipitated by barium chloride in the usual manner, using 10 cc. of a 10 per cent solution of the reagent, and precipitating slowly from a boiling solution. In a series of over forty experiments only two, as mentioned later, showed traces of  $\text{SO}_3$  escaping with the gases of combustion. With the exception of these two, the barium chloride solution through which the gases were passed was added slowly to the bromine solution thus oxidizing any  $\text{SO}_2$  dissolved in the barium chloride solution, and at the same time precipitating the sulfate contained in the solution. Care was taken to boil off all free bromine and, in order to get a precipitate which would settle well, the solution containing it was boiled for at least one-half hour, kept warm for two hours, and usually allowed to stand over night before filtering.

A pressure of 20 atmospheres was used in each experiment and, since practically only 19 atmospheres were delivered from the bomb by release of pressure, it was assumed that the  $\text{SO}_2$  obtained in the absorption apparatus represented only nineteen-twentieths of the  $\text{SO}_2$  in the gases of combustion. A corresponding correction was made in the calculations and  $^{20}/_{19}$ ths of the sulfur found as  $\text{SO}_2$  in the absorption apparatus was taken as the approximate amount formed by the combustion.

It was found that a mixture of pyrites and benzoic acid, even when ground for considerable time in an agate mortar, could not be relied upon to be perfectly homogeneous. This made it difficult to determine the exact weight of pyrite in each combustion, and since our problem concerned only the sulfur as oxides, the total sulfur appearing as oxides after combustion was taken as the basis of our estimations.

As before mentioned, investigators have found that the formation of  $\text{SO}_3$  increases only slightly with increase of pressure, so no determinations were made at different pressures. Thinking, however, that the nitrogen present might have some influence (through formation of nitrogen oxides) on the oxidation of sulfur dioxide, varying percentages of nitrogen were mixed with the oxygen used in the experiments.

Series A, B, and C, Table I, represent preliminary work. No deductions were made for the small amount of sulfur in the oxidizing solution of bromine, so that the results are not so reliable as the later ones. They are cited, however, as confirmatory evidence. In Series A—2 and 3, Table I, traces of  $\text{SO}_3$  were carried from the bomb by the gases of combustion. The sulfate was determined quantitatively but the small amount of  $\text{SO}_2$  absorbed by the barium chloride solution was lost, making the value here slightly low for the sulfur as dioxide.

The small amount of nitrogen, 0.53 per cent, in the bomb gases was obtained from a special oxygen giving by analysis 99.48 per cent pure oxygen. This oxygen was manufactured from chemical sources and not from liquid air, so that the 0.5 per cent impurity may safely be considered nitrogen and not argon. The bomb was filled to 10 atmospheres, pressure released, then filled to 15 atmospheres, pressure again released, and finally filled to 20 atmospheres for the combustion.

Although no great accuracy was attempted in the experiments recorded in the first three series of Table I, yet they show that the ferric oxide formed by combustion of the pyrites in coal does not exert a sufficient catalytic effect to warrant the assumption upon which the correction for the heating value of the fuel is based. They indicate, also, at least one very interesting result, *i. e.*, that with only a small amount of nitrogen present in the bomb the conversion of  $\text{SO}_2$  to  $\text{SO}_3$  is far from complete and is the more incomplete the greater the percentage of sulfur.

After a calibration of the pressure gauge, a series of experiments were made in order to determine more exactly the effect of the nitrogen concentration upon the oxidation of the  $\text{SO}_2$  in the bomb. The manipulation of the apparatus was practically the same as that described in experiments Series A, B, and C, but, for the calculations, blank determinations were run on the oxidizing solution of bromine water in order to ascertain the amount of sulfur. Three such determinations gave respectively 0.00046 g., 0.00041 g., and 0.00046 g. of sulfur per 250 cc. of solution, or 0.00018 g. per 100 cc., and corresponding corrections were made for the amount of the oxidizing solution used in the absorption apparatus.

It was found in the first set of experiments that considerable sulfur remained in the residue after the combustion of the fuel. It was necessary to estimate this in order to calculate the heating value of a gram of sulfur, which is given at the close of this paper. In order to obtain this correction, the fuel, except in Series F, was burned in a platinum capsule, the entire residue fused with sodium carbonate and nitrate, the fusion dissolved in water free from sulfate, filtered, acidified, boiled, and the sulfate determined as usual by precipitation with barium chloride. In Series F of Table I, the sulfur in the ash was much in excess of that obtained in the other residues. The fuel was burned in a comparatively deep nickel capsule in this series and this may account, at least in part, for the amount of unburned pyrites. The sulfur in all the residues from the mixture of benzoic acid and pyrites was higher than that ordinarily obtained from the ash of coal. Coal, however, carries silica which, during the combustion, may unite with the iron of the pyrites to form ferrous silicate, thus displacing the sulfur and effecting its more nearly complete elimination from the ash. When sulfur determinations were made on the residue from the combustion, artificial gas was used as the source of heat for the fusion, and, although the crucible in which the fusion was accomplished was placed in a sheet of asbestos to prevent the products of combustion of the gas from entering the crucible,

yet blanks run in the same manner and with approximately the same height of flame showed the presence of 0.00107 g. of sulfur, and this deduction was made in the calculations.

The results are recorded under Series D, E, and F, Table I, and they show that the amount of nitrogen in the bomb affects materially the relative amounts of the oxides of sulfur formed by the combustion. We see that when the sulfur obtained as oxides represents approximately 6 per cent of the fuel and when 0.53 per cent of nitrogen is present in the bomb gases, the sulfur as  $\text{SO}_2$  is practically twice that as  $\text{SO}_3$ . However, when 6 per cent of nitrogen is present the conversion to  $\text{SO}_3$  is almost complete, the same pressure (20 atmospheres) being used in each case. We

Kolbe, who, in 1846, called attention to the nitric acid formed in explosions of mixtures of hydrogen and oxygen.<sup>1</sup> These investigators found that the nitrogen entering the reaction increased with increase in temperature of the explosion, and that by lowering the temperature to a certain point, no appreciable oxidation of the nitrogen was obtained. Quantitative determinations were made by Bunsen, of the amounts of nitrogen oxides obtained by explosions of mixtures of oxy-hydrogen mixture and air in varying proportions. His results were so accurate that they were recently used for calculations upon the concentration and velocity of reaction between nitrogen and oxygen in the process for the formation of nitrogen oxides by the use of the electric current.

TABLE I—COMBUSTION OF BENZOIC ACID AND PYRITES  
Combustions made at 20 Atmospheres Pressure. Weight of Benzoic Acid Varied from 0.8 to 1.2 Gram

TABLE 1.—ANALYSES OF SULFUR DIOXIDE AND SULFUR TRIOXIDE IN THE GASES FROM THE COMBUSTION OF SULFUR, SULFUR DIOXIDE, AND SULFUR TRIOXIDE IN THE PRESENCE OF AIR, OXYGEN, AND NITROGEN, AND IN THE PRESENCE OF AIR, OXYGEN, AND NIT													
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also see that the degree of the conversion varies with the amount of sulfur in the fuel. In Series E—3 and 4 with a fuel having a sulfur content of approximately 1.5 per cent, the sulfur burning to  $\text{SO}_2$  is a little less than that burning to  $\text{SO}_3$ , while in Series D—1 and 2 with a fuel giving 6 per cent of sulfur as oxides, the  $\text{SO}_2$  is twice the amount obtained as  $\text{SO}_3$ , the conditions being the same in each case. In Series F—5, no water was used in the bomb, and it will be noted that only about one-fourth of the sulfur was obtained as  $\text{SO}_3$ . It may be that, under such conditions, a mist of nitrosyl-sulfuric acid formed, which was decomposed but little by the water from the combustion. If this were true, the nitrogen oxides held in combination would function but once in the oxidation of  $\text{SO}_2$  and, as a result, less sulfur would be obtained as  $\text{SO}_3$ . It indeed seems very probable that the oxides of nitrogen, formed by the heat of combustion of the fuel, function in the oxidation of  $\text{SO}_2$  in a manner somewhat similar to their action in the "lead chamber process" for the manufacture of sulfuric acid.

#### THE FORMATION OF NITROGEN OXIDES BY OXIDATION OF NITROGEN OF THE AIR

The formation of nitrogen oxides and the production of nitric acid by the oxidation of the nitrogen of the air has been observed by many chemists. The earliest record found by the writer is that of Bunsen and

Observations made by Kolbe at a later date showed that when hydrogen is burned in oxygen mixed with a small amount of air, some oxidation of the nitrogen of the air occurs. The results obtained by Kolbe were also observed by A. W. Hoffmann.<sup>2</sup> Investigations made by Zöller and Grete<sup>3</sup> led them to believe that when hydrogen burns in air a small amount of ammonium nitrite is obtained. Later Wright<sup>4</sup> in a series of experiments on the combustion of hydrogen in air, free from ammonia, found no trace of the nitrite mentioned by Zöller and Grete.

Quantitative estimations of the amounts of nitrogen oxides formed by the oxidation of the nitrogen of the air by the explosion of combustible gases under different pressures and with varying proportions of the gases in the mixture were made at later dates by Hempel,<sup>5</sup> Vieth,<sup>6</sup> Salvadori,<sup>7</sup> and Berthelot.<sup>8</sup>

Hempel used in his work an autoclave having a capacity of 28 cc. and lined with platinum. In his first experiments, he burned coal containing 2.8 per cent nitrogen in oxygen made from potassium chlorate

<sup>1</sup> *Annalen der Pharmacie*, **59** (1846), 208-217.

<sup>2</sup> *Chem. Ber.*, **3** (1870), 663.

<sup>3</sup> *Ibid.*, **10** (1877), 2144-2146.

<sup>4</sup> *Ibid.*, **11** (1878), 2146.

<sup>5</sup> *Ibid.*, **23** (1890), 1455-1457.

<sup>6</sup> *Ibid.*, **21** (1888), 695.

<sup>7</sup> *Gazzetta chimica ital.*, **302** (1900), 389-404.

<sup>8</sup> *Compt. rend.*, **130** (1900), 1345 and 1430.

and manganese dioxide. He obtained the results tabulated below and noted that the mass proportion of the gases to one another and to the amount of coal used had a decided influence upon the quantity of nitric acid formed.

## RESULTS OBTAINED BY HEMPEL

Coal Gram	Atmospheres pressure		Nitrogen oxides Cc.
	Air	Oxygen	
0.622	1	9.5	3.0
0.576	1	32.8	3.0
0.599	1	64.2	8.5
0.793	1	72.0	9.0
0.616	1	80.0	7.6
0.622	24	68.0	14.0
0.595	13	79.0	20.5
0.711	92	125.5	5.0
0.683	1	243.0	8.0

Knowing that the nitrogen oxides formed in the above experiments came in part from the nitrogen of the coal, Hempel made a second series of experiments using oxygen and hydrogen in theoretical proportions instead of coal and obtained the following results:

Air	Atmospheres pressure		Nitrogen oxides Cc.
	Oxygen	Oxygen-hydrogen mixture	
1	17.2	25.2	4.8
1	26.0	30.0	6.4
1	53.0	60.0	8.0
1	54.0	118.0	9.0
1	54.0	156.5	10.0

Berthelot made quantitative determinations of nitrogen oxidation in the bomb calorimeter by combustion of carbon and sulfur in an atmosphere of oxygen containing 8 per cent nitrogen at a pressure of 25 atmospheres. He found that with the combustion of 1 g. of amorphous carbon, 0.011 g. of the nitrogen in the

to from 250 to 300 cc., no appreciable amount of nitric acid was lost by this process. The value of the standard alkali used was estimated by titrating it against a standard hydrochloric acid solution already made up in the laboratory. Methyl red was used as the indicator both in finding the value of the standard alkali and in titrating the bomb washings. The alkali required for total acidity minus that required for the sulfuric acid found by precipitation from the bomb washings was taken as the amount necessary to neutralize the nitric acid formed in the bomb.

A number of quantitative determinations are given in Table I, and, when we compare these results with the relation between the sulfur oxides from the same table, it is quite evident that the nitrogen oxides are important factors in the oxidation of  $\text{SO}_2$  in the bomb.

There has been much discussion concerning the reactions which take place between the oxides of nitrogen and  $\text{SO}_2$  when water is present, and the conditions existing in the bomb do not tend to make the reactions less complex. A summary of the investigations made upon this problem, including his own extensive researches along the same line, are given by Lunge.<sup>1</sup>

## COMBUSTION OF COAL IN THE BOMB CALORIMETER

The results obtained by the combustion of the mixtures of benzoic acid and pyrites do not justify the assumption that all sulfur of a fuel necessarily burns to  $\text{SO}_3$  in the bomb calorimeter. This assumption is not correct when oxygen containing a very small amount of nitrogen is used. A coal was then burned under the same conditions as the benzoic acid-pyrites

TABLE II—COMBUSTION OF COAL AND OF MIXTURES CONTAINING NITROGEN COMPOUNDS  
Combustions Made at 20 Atmospheres Pressure: 0.5 cc. Water Used in Bomb in Each Case

EXPERIMENT		MINUTES		GRAMS NITROGEN		GRAMS OF SULFUR				Per cent S on basis of oxides as	Grams $\text{HNO}_3$ from N oxidized in bomb	
		Between emptying and firing bomb	Used in emptying bomb	N by volume in bomb gases before combustion	S in fuel (from $\text{SO}_2$ and $\text{SO}_3$ formed in combustion	In bomb gases before combustion	In fuel	As $\text{SO}_2$ and $\text{SO}_3$	Burning to			
									$\text{SO}_3$	$\text{SO}_2$	In residue	
Series and materials		No.										
G—Coal.	1	15	19	0.53	1.11	0.0432	0.0146	0.0111	0.0108	0.0003	...	97.3 2.7 0.0153
	2	15	18	0.00	1.07	0.4891	0.0146	0.0110	0.0107	0.0003	0.0007	97.3 2.7 0.0321
	1	17	18	0.53	1.83	0.0432	0.0140	0.0187	0.0184	0.0003	0.0003	98.4 1.6 0.0153
H—Coal and pyrites.	1	20	0.53	1.91	0.0432	0.0153	0.0215	0.0204	0.0011	0.0001	0.0001	94.9 5.1 0.0112
	1	16	25	0.53	7.10	0.0432	0.0136	0.0835	0.0537	0.0298	0.0033	64.3 35.7 0.0107
I—Coal and pyrites	1	120	25	0.53	7.17	0.0432	0.0129	0.0737	0.0589	0.0148	0.0048	79.9 20.1 0.0107
	1	18	23	0.53	5.39	0.0432	0.0114	0.0533	0.0139	0.0374	...	29.9 70.1 0.0015
J—Benzoic acid, pyrites and carbamide.	1	120	23	0.53	5.39	0.0432	0.0143	0.0670	0.0212	0.0458	...	31.6 68.4 0.0020
	1	18	25	0.53	6.90	0.0432	0.0598	0.0738	0.0730	0.0008	...	98.9 1.1 0.0173
K—Coal, pyrites and carbamide.	1	19	22	0.53	7.31	0.0432	0.0249	0.0815	0.0584	0.0231	...	71.7 28.3 0.0025
	1	15	15	0.53	6.82	0.0432	0.0168	0.0750	0.0238	0.0492	...	34.4 65.6 0.0025
L—Benzoic acid, pyrites and anthranilic acid.	1	120	25	0.53	6.71	0.0432	0.0179	0.0786	0.0247	0.0539	...	31.4 68.6 0.0018
	1	18	25	0.53	7.65	0.0432	0.0579	0.0784	0.0764	0.0020	...	97.5 2.5 0.0184
M—Coal, pyrites and albumen.	1	15	20	0.53	7.35	0.0432	0.0351	0.0935	0.0931	0.0004	...	99.6 0.4 0.0255
	1	15	25	0.53	4.60	0.0432	0.0210	0.0587	0.0253	0.0304	...	45.4 54.6 0.0026
N—Benzoic acid, pyrites and albumen.	1	120	28	0.53	4.08	0.0432	0.0244	0.0572	0.0262	0.0310	...	45.8 54.2 0.0051
	1	15	25	0.53	7.06	0.0432	0.0626	0.0788	0.0402	0.0386	...	51.0 49.0 0.0051
O—Benzoic acid, pyrites and ammonium carbonate.	1	120	28	0.53	6.99	0.0432	0.0583	0.0727	0.0374	0.0353	...	51.4 48.6 0.0020
	1	15	25	0.53	7.23	0.0432	0.0432	0.0714	0.0700	0.0014	...	98.0 2.0 0.0020
P—Coke and pyrites.	1	120	25	0.53	7.34	0.0432	0.0432	0.0792	0.0772	0.0020	...	97.5 2.5 0.0020

bomb entered into combination with the oxygen, but when sulfur was used instead of carbon only one-eleventh as much nitrogen was oxidized.

The writer estimated the amount of nitric acid in the bomb as follows: The washings which were obtained by carefully rinsing out the bomb were boiled to expel any  $\text{SO}_2$ , cooled, and then titrated for total acidity. Since only a small amount of nitric acid was contained in the washings whose volume amounted

mixtures in order to determine the products formed by the sulfur content. For this purpose a Pittsburgh coal carrying 1.07 per cent of sulfur was used.

The experiments were conducted as previously described and the results are summarized in Series G, Table II. In these experiments almost all the sulfur was found as  $\text{SO}_3$  and they therefore justify the as-

<sup>1</sup> "Manufacture of Sulfuric Acid and Alkalies," Lunge, fourth edition, Vol. 1, pp. 330 to 357 (1913).



sumption with which the sulfur correction on the heating value of coal is concerned.

How, then, are we to account for the almost complete oxidation of the sulfur of coal to  $\text{SO}_3$  with only 0.53 per cent nitrogen in the bomb gases, when, under the same conditions, the mixtures of benzoic acid and pyrites gave a conversion of  $\text{SO}_2$  to  $\text{SO}_3$  which was far from complete. We would infer from the results in Table I that an increased amount of nitrogen oxides was formed.

Titration for the amount of acid in the bomb washings showed a marked increase in the formation of nitric acid over that produced by the combustion of a fuel containing no nitrogen, under the same conditions. The titra ons gave 3.0 cc. of the standard alkali required to neutralize the nitric acid formed in Series G—1 while only 0.3 cc. was required when benzoic acid and pyrites were used. This shows that the nitrogen contained in the fuel is much more efficient in the production of nitrogen oxides than is the nitrogen in the gas with which the bomb was filled. In this case

of the nitrogen present in the bomb gas at the above concentration produced nitric acid. In Series G—2, the nitric acid in the bomb required 6.3 cc. of standard alkali for neutralization. This is about what we would expect since we find, Table III, that the bomb gases with a 6 per cent nitrogen concentration gave, with a nitrogen-free fuel, nitric acid requiring 3.5 cc. of the standard alkali, and this added to the 2.7 cc. required for the nitric acid from the coal, would give us 6.2 cc. of the standard alkali. It will be noted that these results do not justify the assumption made by some that all nitrogen of coal when burned in the bomb calorimeter goes to nitric acid.

If the foregoing conclusions be true, *i. e.*, if the nitrogen in the coal furnishes by combustion of the fuel a very much greater amount of nitrogen oxides than the nitrogen of the commercial oxygen, and if the nitrogen oxides so formed are effective agents in the oxidation of  $\text{SO}_2$ , then it must follow that the sulfur of pyrites, when burned with coal in the calorimeter, will be converted to  $\text{SO}_3$  to a much greater extent

TABLE III—SUMMARY OF RESULTS (COMBUSTIONS AT 20 ATMOSPHERES PRESSURE)

EXPERIMENT Series No.	MATERIALS	PER CENT NITROGEN		% S in fuel (from $\text{SO}_2$ and $\text{SO}_3$ formed in combustion)	SULFUR		Cc stand- ard alkali required for $\text{HNO}_3$ formed
		by volume in bomb gases	in fuel		Grams as $\text{SO}_2$ and $\text{SO}_3$	% as $\text{SO}_3$	
E 3	Benzoic acid and pyrites.	0.53	None	1.40	0.0132	50.8	0.3
E 4	Benzoic acid and pyrites.	0.53	None	1.43	0.0157	56.0	0.2
F 1	Benzoic acid and pyrites.	0.53	None	3.99	0.0371	36.4	0.2
F 2	Benzoic acid and pyrites.	0.53	None	5.76	0.0664	33.2	
D 2	Benzoic acid and pyrites.	0.53	None	6.31	0.0653	30.7	
D 1	Benzoic acid and pyrites.	0.53	None	6.59	0.0760	32.5	
E 1	Benzoic acid and pyrites.	6.00	None	1.56	0.0131	94.7	3.5
E 2	Benzoic acid and pyrites.	6.00	None	2.06	0.0207	93.3	4.3
F 3	Benzoic acid and pyrites.	6.00	None	5.06	0.0612	97.4	3.5
F 4	Benzoic acid and pyrites.	6.00	None	6.01	0.0631	97.6	
D 4	Benzoic acid and pyrites.	6.00	None	6.18	0.0792	99.2	2.9
D 3	Benzoic acid and pyrites.	6.00	None	6.88	0.0712	99.1	
G 1	Coal.	0.53	1.41	1.11	0.0111	97.3	3.0
G 2	Coal.	0.53	1.41	1.07	0.0110	97.3	6.3
H 1	Coal and pyrites.	0.53	1.37	1.83	0.0187	98.4	3.0
H 2	Coal and pyrites.	0.53	1.37	1.91	0.0215	94.9	2.2
N 2	Benzoic acid, pyrites and albumen.	0.53	1.74	4.08	0.0572	45.8	
N 1	Benzoic acid, pyrites and albumen.	0.53	1.74	4.60	0.0557	45.4	0.5
J 1	Benzoic acid, pyrites and carbamide.	0.53	1.15	5.39	0.0533	29.9	0.3
J 2	Benzoic acid, pyrites and carbamide.	0.53	1.15	5.39	0.0670	31.6	0.4
L 2	Benzoic acid, pyrites and anthranilic acid.	0.53	1.53	6.71	0.0786	31.4	0.5
L 1	Benzoic acid, pyrites and anthranilic acid.	0.53	1.53	6.82	0.0750	34.4	0.2
J 3	Benzoic acid, pyrites and carbamide.	0.53	5.60	6.90	0.0738	98.9	3.4
O 2	Benzoic acid, pyrites and ammonium carbonate.	0.53	5.60	6.99	0.0727	51.4	
O 1	Benzoic acid, pyrites and ammonium carbonate.	0.53	5.60	7.06	0.0788	51.0	1.0
I 1	Coal and pyrites.	0.53	1.15	7.10	0.0835	64.3	
I 2	Coal and pyrites.	0.53	1.15	7.17	0.0737	79.9	2.1
P 1	Coke and pyrites.	0.53		7.23	0.0714	98.0	
K 1	Coal, pyrites and carbamide.	0.53	2.24	7.31	0.0815	71.7	
P 2	Coke and pyrites.	0.53		7.34	0.0792	97.5	
M 1	Coal, pyrites and albumen.	0.53	2.76	7.35	0.0935	99.6	5.0
L 3	Benzoic acid, pyrites and anthranilic acid	0.53	5.60	7.65	0.0784	97.5	3.6

2.7 cc. of the standard alkali were required to neutralize the nitric acid formed from the nitrogen in the coal. The amount of coal used in the above experiments was approximately 1 g., and, as the coal contained 1.4 per cent nitrogen, 0.014 g. nitrogen was present in the fuel. The 2.7 cc. of the standard alkali used to neutralize the nitric acid from the coal are equivalent to 0.0031 g. of nitrogen since each cubic centimeter of the standard alkali contained 0.00457 g. of potassium hydroxide. In this case, then, 0.0031 divided by 0.014, or about 22 per cent of the nitrogen of the coal was oxidized to nitric acid. The gas used in the bomb, Series G—1, contained 0.53 per cent nitrogen. Since the capacity of the bomb was 350 cc. this, at 20 atmospheres pressure, would be equivalent to 0.0432 g. of nitrogen. The 0.3 cc. required to neutralize the acid formed from this nitrogen is equivalent to 0.00034 g. of nitrogen, so a little less than 1 per cent

than when burned with benzoic acid. Accordingly, a test of these conclusions was made, using for the combustion the same coal mixed with sufficient pyrites to give a sulfur content corresponding to that in Series E—3 and 4, and burned in oxygen containing a nitrogen concentration of 0.53 per cent. The results substantiate our conclusions as is shown by Series H, Table II.

To test our conclusions still further, a second mixture of coal and pyrites was made, using the same coal as in Series H, and adding enough pyrites to give a sulfur content corresponding approximately to that in Series D—1 and 2, Table I, in which the benzoic acid was used with the pyrites. These results are recorded in Series I, Table II, and when we compare them with Series D—1 and 2, it at once becomes evident that our conclusions hold as to the effect produced upon the extent of oxidation of  $\text{SO}_2$  by the nitrogen oxides obtained by the combustion of the coal.

INFLUENCE OF NITROGEN-CONTAINING SUBSTANCES,  
OTHER THAN COAL, ON THE OXIDATION OF  $\text{SO}_2$   
WHEN BURNED IN THE BOMB CALORIMETER

We have found that when coal is burned in a calorimeter its nitrogen forms oxides which have a marked influence on the extent of the oxidation of the  $\text{SO}_2$ . Can we say as much concerning other nitrogen-containing bodies? Coal by distillation yields ammonia; hence an amido compound, carbamide,  $\text{CO}(\text{NH}_2)_2$ , was mixed with benzoic acid and pyrites in sufficient quantity to furnish 1.15 per cent nitrogen, the amount furnished by the pyrites-coal mixture in Series I, and this mixture burned under the same conditions as the preceding series. The results are tabulated in Series J—1 and 2, Table II. These experiments show that with a small amount of carbamide in the fuel (sufficient to furnish 1.15 per cent nitrogen) there is very slight if any change in the extent of oxidation of the  $\text{SO}_2$  from that in Series D—1 and 2, Table I, in which the fuel contained no nitrogen and carried even a slightly greater percentage of sulfur; also, there was no increase in the amount of nitric acid formed, over that obtained by the combustion of the fuel containing no nitrogen. However, when sufficient carbamide was added to furnish 5.6 per cent nitrogen in the mixture of benzoic acid and pyrites, a decided change in the extent of the oxidation of  $\text{SO}_2$  was obtained, as is shown in Series M—3, and a corresponding change in the amount of nitric acid formed.

The calorific value of benzoic acid per gram is less than that of the coal used, therefore the heat generated per gram of fuel in Series J—1 and 2 was less than that in Series I. Since it is known that temperature affects the formation of nitrogen oxides, it was thought best to make another test. In order to make such a test at a temperature equal approximately to that in the combustion of Series I, there was added to the mixture in that series as much nitrogen in the form of carbamide as was present in the coal, and the effect upon the oxidation of the  $\text{SO}_2$  was determined. The results tabulated, Series K, Table II, show only a slight change in the percentage of sulfur oxidized to  $\text{SO}_2$  from that in Series J.

The nitrogen of carbamide proved to have a much weaker influence upon the percentage of sulfur oxidized to  $\text{SO}_2$  than the nitrogen of coal, and the writer later found from the work of J. A. Fries, U. S. Dept. of Agriculture, that this is what might have been expected.

Fries found that the quantity of nitrogen oxidized varies with the substance burned, the total heat generated, and the quantity of nitrogen in the bomb. The averages of a large number of experiments are given on pages 29 and 30 of his report<sup>1</sup> from which we learn that the nitrogen behaves very differently in different substances as is seen from his data which is quoted in part:

Substance burned	Percentage of nitrogen of sample oxidized to nitric acid
Hair and dandruff	43.02
Gelatin	5.83
Gelatin with alcohol	19.75
Urine with cellulose	0.00
Linsseed meal	3.37

<sup>1</sup> Bulletin 94 (1902), Bureau of Animal Industry, U. S. Dept. of Agriculture.

Fries accounts, at least in part, for the above results by assuming that most of the nitrogen oxide is formed at the contact with the ash or skeleton of the substance burned, that is, at the point of greatest chemical activity. Since a large number of chemical changes take place at that point in a very short time, it may be that the product formed will possess such an attraction for the nitric acid that it will not escape to the walls of the bomb. This he believes to be true in the case of urea and other substances where the ash is somewhat alkaline. If such conditions exist it is quite evident that no change in the percentage of sulfur oxidized to  $\text{SO}_2$  would occur.

It was next thought advisable to try the effect of some other nitrogen-containing substances upon the oxidation of the  $\text{SO}_2$  when pyrites was burned in the calorimeter. For this purpose anthranilic acid ( $\text{C}_6\text{H}_4\text{NH}_2\text{COOH}$ ), egg albumen, and ammonium carbonate,  $(\text{NH}_4)_2\text{CO}_3$ , were used. The results of the experiments together with the conditions under which they were made are recorded in Table II.

Series L corresponds to Series J, in which the fuel contained carbamide, except that anthranilic acid was used as the nitro-body and the amount present in Experiments 1 and 2 was sufficient to give to the fuel a nitrogen content of 1.5 per cent. The results show but slight change in the extent of oxidation of the  $\text{SO}_2$  from that in Series J—1 and 2, and little increase in the amount of nitric acid formed.

In Series L—3, sufficient anthranilic acid was added to the mixture to give 5.6 per cent nitrogen in the fuel; and, as in Series J—3, a decided change occurred in the percentage of sulfur oxidized to  $\text{SO}_2$ , this change being again accompanied by a corresponding increase in the amount of nitric acid formed in the bomb.

Series M corresponds to Series I except that sufficient egg albumen was added to give, with the nitrogen of the coal, 2.76 per cent nitrogen in the fuel. Here the oxidation of the sulfur to  $\text{SO}_2$  was practically complete while in Series I not more than 80 per cent of the sulfur burned to  $\text{SO}_2$ . The weight of the fuel pellet in this experiment was seven-sixths of that in Series I, and the increased amount of heat may account in part for the conversion of the sulfur to  $\text{SO}_2$  but it seems probable that the albumen was also an agent in the change of extent of oxidation.

Series N represents a further test of the egg albumen in forming nitrogen oxides and, consequently, in increasing the percentage of sulfur obtained as  $\text{SO}_2$ . The fuel consisted of egg albumen and pyrites in the same proportions as for Series M, and benzoic acid corresponding to the amount of coal in that series. The results obtained, Table II, do not show a change in oxidation of sulfur comparable to that obtained with coal containing a smaller percentage of nitrogen in the fuel.

The mixture of ammonium carbonate, benzoic acid, and pyrites, Series O, Table II, contained 5.16 per cent nitrogen and, although the results obtained by combustion of the fuel show considerable effect upon the extent of oxidation of  $\text{SO}_2$ , yet the change is not nearly so marked as in experiments, Series J—3 and Series

L—3, in which the same percentage of nitrogen was present in the fuel.

It will be noted that the nitrogen content of a fuel consisting of benzoic acid, pyrites, and a nitrogen body, other than coal, when burned in the bomb has much less effect upon the conversion of  $\text{SO}_2$  to  $\text{SO}_3$  than has the nitrogen of coal. This is accounted for by the following facts: (1) the quantity of nitrogen oxides formed varies with the nature of the substance burned; (2) the weight of the fuel pellet used was approximately the same in each case, and since the calorific value of the coal is greater than that of the mixture of benzoic acid, pyrites, and nitrogen body, the greater heat evolved by the combustion of the coal would of itself produce a slightly greater oxidation of nitrogen; (3) the physical conditions under which the components of coal exist as well as the compounds present can be approximated only by artificial mixtures.

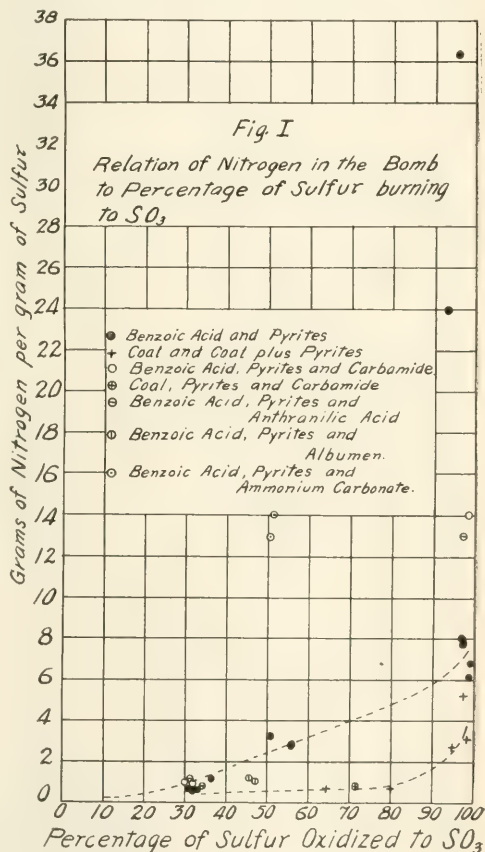
As an example of the small amount of nitrogen oxidized by the combustion of the pyrites mixtures containing nitrogen compounds, let us consider Experiment 3, Series O, to which ammonium carbonate was added. In this experiment the weight of nitrogen in the fuel was 0.0579 g. and that of the nitric acid formed was 0.0184 g. The weight of nitric acid formed in the bomb by the combustion of a non-nitrogenous fuel with only 0.53 per cent nitrogen concentration in the bomb gases was 0.0015 g. The amount of nitric acid formed by the oxidation of the nitrogen in the fuel was 0.0184 g. — 0.0015 g., or 0.0169 g. This quantity of nitric acid is equivalent to 0.0038 g. in terms of nitrogen, and since the fuel contained 0.0579 g. of nitrogen, a little more than 6.5 per cent was oxidized by the combustion, while in the corresponding experiment where coal was used, approximately 22 per cent of the nitrogen content burned to nitrogen oxides.

Since the volatile compounds of coal yield ammonia by distillation, it seems probable that their action in the bomb calorimeter would be somewhat similar to the nitrogen content of carbamide and anthranilic acid, both of which contain the amido-group ( $\text{NH}_2$ ). The decreased oxidation of the nitrogen in these compounds below that of the nitrogen in coal would lead us to believe that it is the fixed nitrogen of coal which is the more efficient in the formation of nitrogen oxides in the bomb. If this be true, the nitrogen of coke should give a greater oxidation of  $\text{SO}_2$  than the nitrogen of coal. To test this assumption a mixture of coke and pyrites was made corresponding in sulfur content to Series I, and burned under the same conditions. The nitrogen was not determined in the particular sample of coke but the general assumption is that coke carries about 50 per cent of the nitrogen of the coal. Almost complete oxidation of the sulfur to  $\text{SO}_3$  occurred as is shown by Series P, Table II. As only partial conversion of  $\text{SO}_2$  to  $\text{SO}_3$  occurred in Series I, it seems very probable that our assumption as to the activity of the fixed nitrogen in coal is correct.

The results obtained by introducing a nitrogen carrier into the fuel for combustion are in agreement

with our former evidence concerning the effect of the nitrogen oxides formed in the bomb upon the extent of oxidation of the  $\text{SO}_2$ . With this confirmation of our former results, we believe we have established that the nitrogen oxides formed in the bomb have a marked effect upon the oxidation of the  $\text{SO}_2$ . We therefore feel justified in calling attention to the possibility of error in the correction for sulfur on the calorific value of a fuel carrying little or no nitrogen, and in estimating its sulfur content by precipitation from the bomb washings, when a very small concentration of nitrogen is present in the bomb gases.

The varying effects of the nitrogen content of the bomb gases, of the coal, and of the pyrites mixtures

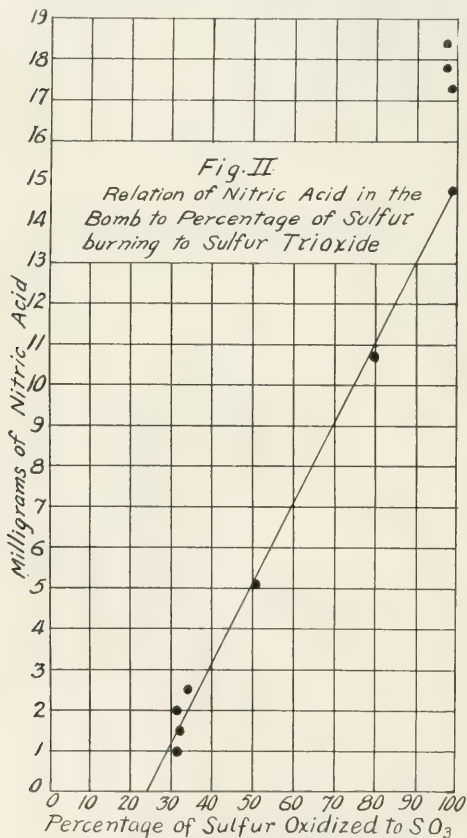


upon the oxidation of  $\text{SO}_2$  through the action of nitrogen oxides formed by combustion of the fuel in the bomb calorimeter are shown graphically in Fig. I. The grams of nitrogen present in the bomb per gram sulfur are plotted with reference to the percentage of sulfur oxidized to  $\text{SO}_3$ . These results, in general, indicate increased percentage of  $\text{SO}_3$  with increased amount of nitrogen, and, where several results have been obtained using the same fuel, as in the mixtures of ben-



zoic acid and pyrites, and in the combustions with coal as nitrogen-carrier, the results indicate a fairly regular curve, the curve depending upon the substance burned.

In order to bring out still more clearly the oxidizing action of the nitrogen oxides formed in the bomb, the results of nine titrations for nitric acid, together with the percentage of sulfur appearing as  $\text{SO}_3$ , are plotted in Fig. II. These quantitative estimations of nitric acid were made as previously described. Only those results are plotted which were obtained when the fuel for combustion contained 6 to 8 per cent sulfur and a sufficient quantity burned to produce 0.06 g.



to 0.08 g. of sulfur as oxides. Since the nitrogen oxides formed convert only a certain amount of  $\text{SO}_2$  to  $\text{SO}_3$ , depending upon conditions existing in the bomb, it is evident that to represent properly the oxidizing effect graphically, the percentage of sulfur in the fuel and the weight of the fuel pellet burned should both be constants. This is not the case in our work. The limits selected above restrict us to a few experiments whose initial conditions are in sufficiently close agreement to give concordant results. Fig. II represents the relation existing between the percentage

of  $\text{SO}_2$  and the weight of nitric acid formed in the bomb under the conditions of the experiment.

#### CONCLUSIONS CONCERNING ESTIMATION OF THE SULFUR CONTENT OF A FUEL BY COMBUSTION IN A CALORIMETER AND PRECIPITATION OF THE SULFATE FROM THE BOMB WASHINGS

None of the experiments tabulated in this paper show a complete absence of  $\text{SO}_2$ , yet they do warrant the conclusion that the sulfur content of a fuel may be determined approximately by combustion in oxygen in a bomb calorimeter and subsequent precipitation of the sulfate from the bomb washings, provided certain conditions are fulfilled. In our work, favorable results, on a fuel carrying no nitrogen, were obtained in a bomb of 350 cc. capacity, at a pressure of 20 atmospheres, with 6 per cent nitrogen concentration in the bomb gases before ignition when the fuel contained as much as 7.0 per cent sulfur. We have shown that the nitrogen content of coal burns in part to nitrogen oxides and that these tend to oxidize any  $\text{SO}_2$  to  $\text{SO}_3$ . It is then evident that with such a fuel the nitrogen concentration in the bomb gas, and the pressure, either or both, may be made less than that above stated and still have practically all sulfur converted to  $\text{SO}_3$ , the limits of such decrease being determined in part by the amount of nitrogen oxides formed by combustion of the fuel. On the other hand, if a fuel containing a very high percentage of sulfur be burned in the calorimeter with the same concentration of nitrogen in the bomb, the pressure will have to be increased if the sulfur be obtained as  $\text{SO}_2$ . This increase would tend not only to complete the oxidation of the sulfur but also to increase the formation of nitrogen oxides which would oxidize  $\text{SO}_2$ .

This is in accord with the findings of A. C. Fieldner, of the Bureau of Mines, Pittsburgh, Pa.<sup>1</sup> Fieldner burned a coal-pyrites mixture containing 25 per cent sulfur, in a calorimeter, at 18 atmospheres pressure, and upon opening the bomb detected  $\text{SO}_2$ . At a pressure of 30 atmospheres almost all the sulfur was obtained as  $\text{SO}_3$ .

It must be remembered that the result obtained for sulfur by the method previously described is not exact and will usually be a little below the true value. The fuel used by the writer in experiments, Series G and H, shows a loss of 2 to 5 per cent of sulfur content by estimation from the bomb washings, and similar low values are recorded by Parr, Wheeler, and Berolzheimer,<sup>2</sup> and by E. E. Somermeier.<sup>3</sup> Undoubtedly these low values, as shown by this paper, are due to loss of sulfur as  $\text{SO}_2$ .

#### TIME A FACTOR IN DETERMINING RATIO OF SULFUR OXIDES IN THE BOMB

Another point of interest noticeable in the results of the experiments tabulated in this paper is the effect of time upon the conversion of  $\text{SO}_2$  to  $\text{SO}_3$ . In several instances, Tables I and II, two groups of experiments were made, the only factor changed in each group

<sup>1</sup> Technical Paper No. 26, Bureau of Mines, p. 10, note H.

<sup>2</sup> THIS JOURNAL, 1 (1909), 689.

<sup>3</sup> Professional Paper No. 48, U. S. Geological Survey, p. 277.

being that of the time intervening between the firing and emptying of the bomb. Usually the results show a greater oxidation of  $\text{SO}_2$  when the bomb stood two hours than when it was emptied fifteen minutes after firing. However, this did not always hold true. Such a change in the oxidation of the  $\text{SO}_2$  is what we would expect if the nitrogen oxides function here somewhat as in the manufacture of sulfuric acid.

#### THE HEATING VALUE OF SULFUR AS PYRITES

The heating value of sulfur as pyrites has been determined by combustion in a bomb calorimeter, and reported by E. E. Somermeier.<sup>1</sup> He found that some of the sulfur remained in the ash and that a small amount escaped with the bomb gases as  $\text{SO}_2$ . He made corrections on the calorific value for the sulfur as  $\text{SO}_2$  and for that in the ash, assuming the latter to exist as ferrous sulfide ( $\text{FeS}$ ), and obtained an average value of 4957 calories per gram sulfur. On page 564 of the journal containing the above-mentioned report, the seven results given for the calorific value of pyrites per gram lie between 2480 and 2686 calories, that is, between 4663 and 5049 calories per gram sulfur; however, the four values selected as being most probable are in very close agreement.

In connection with the experiments made to determine the relation existing between the oxides of sulfur in the bomb, a number of calorific estimations were made by the writer with special reference to the heating value of sulfur as pyrites. A calibrated Beckmann thermometer was obtained from the U. S. Bureau of Standards. The thermometer was graduated to  $0.01^\circ \text{C}$ . and no attempt was made to take readings closer than  $0.005^\circ$ . The water used in the calorimeter plus the water equivalent of the apparatus was equal to 2120 grams, so an error of  $0.003^\circ$  in the temperature reading would make a difference of six calories. In two of the calculated results, less than 0.02 g. of sulfur was present in the fuel and an error of six calories on 0.02 g. would be equivalent to 300 calories per gram sulfur. The sulfur obtained as oxides by combustion and that in the ash was taken as the basis of the calculations, and the results obtained are subject to any errors which may have been made in those determinations.

Grams of sulfur as pyrites	Calories corrected for $\text{FeS}$ and $\text{SO}_2$	Calories per gram S
0.0779	389	4993
0.0779	390	5007
0.0177	82	4632
0.0145	67	4621
0.0769	388	5046
0.0614	323	5260
0.0738	382	5176
0.0794	402	5062

The average value of sulfur as pyrites burning to  $\text{SO}_3$  is, from above results, 4975 calories.

In obtaining the above values, corrections were made for the iron wire fuse, for the sulfur as  $\text{SO}_2$  in the bomb gases, and for the sulfur in the ash, assuming that in the residue to exist as ferrous sulfide. The corrections applied are those given by Somermeier in the aforementioned article and are calculated from values given in the third edition of Ostwald's "Grundriss der Allgemeinen Chemie."

#### SUMMARY

The aim of this investigation was to determine whether or not the correction made for sulfur on the heating value of a coal as obtained by combustion in a bomb calorimeter is justifiable, but since this correction involved the assumption that the sulfur of the fuel burns completely to  $\text{SO}_3$  in the calorimeter, the real problem concerned the relative quantities of sulfur as  $\text{SO}_2$  and  $\text{SO}_3$  in the bomb, and the conditions which affect them. In connection with the experiments necessary for the above study, it was one purpose to ascertain the accuracy of sulfur estimations on a fuel by combustion in the bomb and subsequent precipitation of the sulfate from bomb washings; also to obtain data from which to calculate the heating value of sulfur as pyrites.

I—We have quoted from other investigators results which lead us to believe that pressure alone cannot account for the complete conversion of  $\text{SO}_2$  to  $\text{SO}_3$  in an atmosphere of oxygen.

II—We have established by a number of experiments that when the chief sulfur compound of coal, pyrites, is burned with a non-nitrogenous fuel in the calorimeter in an atmosphere of oxygen under pressure, a fairly stable condition results. This condition is intermediate between the practically complete conversion to  $\text{SO}_3$  existing under the conditions of equilibrium at room temperatures, and the almost total absence of  $\text{SO}_3$  characteristic of combustions taking place without a catalyst to convert the  $\text{SO}_2$  to  $\text{SO}_3$  as the temperature drops. The relative amount of sulfur appearing as  $\text{SO}_3$  increases to a marked degree with increasing amount of nitrogen oxides formed in the bomb, but does not depend to a measurable extent upon any catalytic effect of the ash (see Table III).

We have also quoted authorities showing that the amount of nitrogen oxides formed with a given concentration of nitrogen in the bomb increases with increasing pressure and with the heat of combustion of the fuel.

III—Our experiments show that the nitrogen of coal is much more efficient in forming nitrogen oxides than is the nitrogen of the bomb gases. This, in connection with the fact that in ordinary work the nitrogen concentration in the bomb gases before ignition is at least 5 per cent, accounts for the almost complete oxidation of the sulfur of coal to  $\text{SO}_3$ .

IV—Not only have we found that a change in the oxidation of sulfur is produced by different amounts of nitrogen in the bomb gases and by that in a coal, but we have confirmed these observations by introducing a nitrogenous material into a non-nitrogenous fuel, and found that, with combustion, a change occurred in the extent of oxidation of the  $\text{SO}_2$ .

V—From our results we have drawn conclusions as to the feasibility of estimating the sulfur content of a fuel by combustion in a bomb calorimeter and precipitation of the sulfate from the bomb washings, and have found that approximate results may be obtained from non-nitrogenous substances carrying less than 0.08 g. of sulfur in the fuel burned, at 20 atmospheres

<sup>1</sup> J. Am. Chem. Soc., 26 (1900), 555-568.

pressure, when a nitrogen concentration of 6 per cent is present in the bomb gases. With coal, to which sufficient pyrites had been added to furnish a sulfur content of 7 per cent, only about three-fourths of the sulfur was obtained as  $\text{SO}_2$  when a gram of the fuel was burned at 20 atmospheres pressure, with 0.53 per cent nitrogen by volume in the bomb gases. Under these conditions, estimation of the sulfur content of the fuel from the bomb washings would be much in error. However, with a greater percentage of nitrogen in the bomb gases and at a higher pressure, satisfactory results may be obtained.

VI—We have calculated the heating value of sulfur as pyrites burning to  $\text{SO}_3$ , applying the proper corrections, and have found that the average of our results gave us 4975 calories per gram sulfur.

VII—The corrections prescribed in the proposed Standard Method<sup>1</sup> for the oxidation of sulfur in coal in a bomb calorimeter are shown to be correct only within certain limits.

In the usual procedure, when coal with less than 2 per cent of sulfur is burned in a bomb calorimeter from which the initial charge of air is not removed by rinsing out with oxygen, there will be sufficient formation of oxides of nitrogen to ensure the oxidation of almost all the sulfur to  $\text{SO}_3$ . Under these conditions the corrections prescribed by the committee are proper. If coals are high in sulfur there may be a material amount of the sulfur left as sulfide in the ash and as  $\text{SO}_2$  in the gas. If oxygen of high purity is used and the air in the bomb blown out, as recommended by the Committee on Coal Analysis, so that the concentration of nitrogen in the bomb may be only a fraction of 1 per cent, and if a fuel free from nitrogen is being burned, then only a small amount of oxides of nitrogen will be formed, and even if the fuel contain only 2 per cent sulfur, only a part (sometimes only one-half) of the sulfur will appear as  $\text{SO}_3$ .

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#### ETHYL ESTER OF LINOLIC TETRABROMIDE AS A PRODUCT IN THE ANALYSIS OF COTTONSEED OIL<sup>2</sup>

By LEROY S. PALMER AND PHILIP A. WRIGHT

Received July 13, 1914

In the course of some studies of the composition of cottonseed oil, in which we were isolating the unsaturated acids according to the method of Tortelli and Ruggeri,<sup>3</sup> *i. e.*, making use of the solubility of their lead soaps in ether, and eventually recovering the linolic acid as the tetrabromide, we obtained instead large clustering needles melting sharply at 58–58.5° C.<sup>4</sup> The crystals, in addition, showed a much greater solubility in ninety-five per cent alcohol, glacial acetic acid, petroleum ether, etc., than linolic tetrabromide, from all of which solvents the crys-

tals could be recovered in the same form and with the same melting point.

The new compound was very readily shown to be a bromide; and its melting point was so strikingly similar to the melting point of the tetrabromide of the isomeric telfairic acid of Thoms,<sup>1</sup> *i. e.*, 57–58° C., that it suggested the presence of a similar, heretofore undiscovered acid in cottonseed oil.

Attempts to determine the molecular weight of the low-melting bromide by the titration method of Farnsteiner<sup>2</sup> showed, however, that it had no neutralization value. Molecular weight determinations by the cryoscopic method in glacial acetic acid were also of little value, the results varying between 600 and 700, although great care was taken to exclude moisture.<sup>3</sup>

Ultimate analysis of the low-melting bromide gave the following results:

Determination No.	Bromine Per cent	Hydrogen Per cent	Carbon Per cent	Oxygen (by diff.) Per cent
1.....	51.10	6.064	36.18	
2.....	50.01	5.924	38.97	
3.....	50.56	5.795	38.56	
4.....	50.94	6.012	38.92	
Average.....	50.63	5.95	38.16	5.24
Calculated for linolic tetrabromide.....	53.30	5.36	35.99	5.35

The bromine content was determined on separate samples. Since methods of determining the bromine in compounds of this character are not commonly described in the literature, the method used by us may be of interest at this point.

The substance<sup>4</sup> was dissolved in 95 per cent alcohol, a small stick of KOH added, and the solution boiled under a reflux for one hour. The hot alkaline solution was washed out into a beaker with hot water and the solution diluted to 300 or 400 cc. with water. The beaker was then allowed to stand on the steam bath until most of the alcohol was dispelled. A slight excess of  $\text{HNO}_3$  was added, and heating continued until the fatty acids rose to the top in a clear layer. The solution, which was not allowed to be too concentrated at this point, was then cooled and washed with water and ether into a separatory funnel. It was then shaken carefully with ether, and the aqueous layer drawn off. The ether extract was washed carefully several times with fresh water, the washings being added to the first portion drawn off. The combined aqueous solutions were then heated on the steam bath until the ether was dispelled, care being taken to use a very gentle heat to avoid spattering. The solution was then evaporated to 250–300 cc. and the bromine determined in this solution by precipitating with  $\text{AgNO}_3$ . The determination was carried out from this point in the usual way for determining AgBr.

A comparison of the analyses obtained with the calculated composition of linolic tetrabromide shows that the low-melting bromide has a lower content of bromine and oxygen and a higher content of car-

<sup>1</sup> "Report of Committee on Coal Analysis," THIS JOURNAL, 5 (1913), 526–527; Technical Paper No. 8, Bureau of Mines, p. 15.

<sup>2</sup> The greatest part of the investigation here reported is taken from the Thesis presented by Philip Anson Wright to the Faculty of the Graduate School of the University of Missouri in 1913, in partial fulfillment of the requirements for the degree of Master of Arts.

<sup>3</sup> L'Orcosi, April, 1900; Lewkowitsch, "Oils, Fats and Waxes," Vol. I, p. 447 (1909 edition).

<sup>4</sup> Linolic tetrabromide melts at 113–115° C.

<sup>1</sup> Arch. d. Pharm., 238 (1900), 48.

<sup>2</sup> Zeit. f. Untersuch. Nahr. u. Genussm., 3 (1899), 1.

<sup>3</sup> Stirring was accomplished by means of a magnetically propelled stirrer.

<sup>4</sup> Approximately 0.1 g. of the bromide was used, and an excess of the amount of KOH required to combine with the bromine.



bon and hydrogen. As any variation in the number of bromine and oxygen atoms of linolic tetrabromide would make much greater variations in their respective percentages than are found for the low-melting bromide it was apparent that whatever difference existed between the composition of the two compounds must lie in the number of carbon and hydrogen atoms.

Calculation of formulae from the ultimate analyses indicated a very close agreement of the low-melting bromide with the formula for ethyl-bromo-linolate,  $C_{17}H_{31}Br_4COOC_2H_5$ , as is shown below:

	Calculated for $C_{17}H_{31}Br_4COOC_2H_5$	Found for low- melting bromide
Carbon.....	38.22	38.16
Hydrogen.....	5.78	5.95
Oxygen.....	5.09	5.35
Bromine.....	50.97	50.53

By taking particular analyses even closer agreement is obtained. The conclusion, therefore, seemed justified that the low-melting bromide is merely the ethyl ester of linolic tetrabromide.

In order to verify this conclusion, ethyl-bromo-linolate was prepared from linolic tetrabromide according to the method of Reformatsky<sup>1</sup> for preparing ethyl linolate from linolic acid. The tetrabromide was dissolved in absolute ethyl alcohol and dry HCl gas passed in for an hour. The product which resulted was crystallized out. After purification it showed all the properties, including the melting point of  $58-58.5^\circ C.$ , of the compound obtained from cottonseed oil.

It is probably a mere coincidence that the ethyl ester of linolic tetrabromide has a melting point so nearly identical with the melting point of the tetrabromide of the isomeric telfairic acid. It is possible, however, that Thoms' work on the unsaturated acids of kœme oil requires repetition. It was our intention to do this, but we were unable to secure any of the oil in this country.

The cause of the production of the ethyl ester instead of the ordinary linolic tetrabromide in our studies of cottonseed oil has been the object of much speculation. We have given the matter some study without, however, being able to arrive at any definite conclusions.

As previously stated, the unsaturated acids were isolated from the oil according to the method of Tortelli and Ruggeri, by making use of the ready solubility of their lead soaps in ether. The lead soaps thus obtained were decomposed with dilute HCl, the ether solution of the acids washed free from HCl with water, and the fatty acids brominated directly in this solution at a low temperature, using liquid bromine. Excess bromine was washed out with dilute sodium thiosulfate solution. The ether was then washed with water, dried over fused  $CaCl_2$ , decanted, evaporated at a low temperature, and the liquid mixed bromides treated with petroleum ether (b. p.  $30-50^\circ C.$ ). The oleic and linolic bromides were thus roughly separated, the latter being but little soluble in this solvent at a low temperature. The insoluble tetrabromide was recrystallized from alcohol. The

ethyl ester was obtained while using the above procedure.

Without describing our investigations in detail, which included many variations in the method of bromination, amount of HCl used in decomposing the lead soaps, etc., it may be stated that apparently the step in the isolation that determines the character of the linolic acid end product is the solution of the lead soaps in ether. When the mixed lead soaps of the cottonseed oil acids are allowed to stand under the ether for 48 hours or more before filtering off and decomposing with HCl, the ether takes on a carmine-red color. This color is completely destroyed when the lead soaps are decomposed with HCl. It seems almost assured, however, that the changes that result in the ultimate production of the ester instead of the ordinary tetrabromide are associated in some way with the production of this red color. Whether a definite chemical reaction takes place at this point was not determined, although such a condition seems very probable. That the reaction was sometimes only partially complete was shown in a number of test cases where the lead soaps were allowed to stand for varying lengths of time under ether, with the result that the ultimate product was a mixture of linolic tetrabromide and the ester, crystals of each being obtained. The ester usually crystallized out first from a mixed alcoholic solution.

The foregoing results present several points of interest. In the first place it appears that some care is required not to allow the lead soaps to stand under ether, in isolating the unsaturated acids of cottonseed oil by the lead soap ether method, if the product desired is ordinary linolic acid or its bromide. In the second place there is opened up a field of new products of the unsaturated acids, namely the esters of the bromides. Heretofore esterification has been confined to the acids themselves.<sup>1</sup>

We have prepared a few of these bodies, namely, methyl-bromo-linolate and the methyl and ethyl esters of oleic dibromide. We found the methyl ester of linolic tetrabromide to crystallize from alcohol in white glistening plates resembling the ethyl ester. The slightly impure crystals melted between  $50^\circ$  and  $56^\circ C.$  The two esters of oleic dibromide were found to be yellow oils, very soluble in most solvents, but very little soluble in their corresponding alcohols saturated with HCl gas.<sup>2</sup>

At present actual analysis of cottonseed oil for linolic acid falls far short of the theoretical value indicated by the iodine value of the oil or the mixed unsaturated acids.<sup>3</sup> It is hoped that the ease with which esters of the bromides of the unsaturated acids are formed, especially linolic acid, may eventually be of value in clearing up the composition of cottonseed oil.

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<sup>1</sup> With the exception of the ethyl ester of hexabromolinolenic acid which has been prepared by brominating the ethyl ester of  $\alpha$ -linolenic acid.

<sup>2</sup> The esters of the bromo-linolates are very soluble in alcohol saturated with HCl. Attempts to make use of this difference for the quantitative separation of oleic and linolic acids have, however, not proved successful.

<sup>3</sup> Compare Lewkowitsch, Vol. II, p. 157 (1909 Edition).

<sup>1</sup> Beilstein, "Handbuch. der Organ. Chem.," Vol. I, p. 536

# ENZYMES OF *ASPERGILLUS ORYZAE* AND THE APPLICATION OF ITS AMYLOCLASTIC ENZYME TO THE FERMENTATION INDUSTRY

By JOKICHI TAKAMINE

Received June 8, 1914

## HISTORY

*Aspergillus oryzae*, an insignificant species of fungi, belonging to the genus *Aspergillaceae*, plays an important role in the national economy of Japan, on account of the particular enzymes it generates during its growth. Other species of the same genus are also largely employed for production of various dietary articles in almost all countries of the Orient besides Japan. Nevertheless, its utilization in Occidental countries is singularly lacking. Calmette and Bodin's investigation on amylomyces with a view to utilizing it in the spirit industry is an isolated instance in Europe, and their process, known as the amylo-process, has been in operation in France since 1891.

In 1891, I made an arrangement with the Distilling & Cattle Feeding Co., of Peoria, Ill., and carried out on a practical scale the application of the *Aspergillus oryzae* to the American Distillery. My experiments, which ran for a couple of months on a 2000 bushel scale at the Manhattan Distillery, were partially successful, but unfortunately the process did not attain general recognition of its merit, because it still lacked means to overcome various impediments due to trade conditions and difficulties in adapting the process in the new field of application. I did not forsake the investigation after this first trial, but became even more enthusiastic about perfecting the method. Improvement after improvement was added and I now believe that I can soon demonstrate its usefulness.

For many centuries *Aspergillus oryzae* has been employed in Japan for varied purposes: Sake or rice beer, Soy and Miso are the products which are made by the use of this fungus. The fermentation of Sake for the fiscal year of 1912 contributed to the national treasury the goodly sum of \$41,974,630 revenue. The tax on the production of Soy (Bean sauce) amounted to \$2,048,141. The total cost of both and other articles produced by aid of the fungus in question is put at an aggregate of \$200,000,000. It will thus be seen how important a role the fungus is playing in the national economy of Japan. If we add to the above statement the products and cost of the articles which are put out through the useful services of this fungus, or other species, rendered in all the countries of the Orient, the grand total is an enormous amount. Curiously enough this tiny and important hustler has scarcely attracted attention in the Occident, and this fact made me determine to work for its introduction to industrial use in the United States.

Scientifically, *Aspergillus oryzae* has attracted the attention of Occidental investigators as far back as 1875. Prof. Kozai, of Tokyo Imperial University, reviewed<sup>1</sup> the literature regarding the early investigations on the subject of *Aspergillus oryzae* and its industrial applications, and gives credit to Hoffmann and Korshelt as the first writers upon the subject.

Korshelt<sup>1</sup> made an important contribution to the knowledge of the fungus in Europe. His report was upon Sake fermentation with special reference to an amyloclastic enzyme which occurs in the culture of the fungus on rice and which he named Eurotius. In his "Chemistry of Sake Brewing," Atkinson discusses the function of the enzyme just named. The fungus was then known as *Eurotium oryzae*, being first identified by Ahlburg in 1876 but Cohn later investigation led to renaming it *Aspergillus oryzae*.<sup>2</sup> It was re-examined by Bosgen, Schröter and later Wehmer who gave full morphological descriptions of it. O. Kellner and his pupils' investigations on invertase amylase and maltase are worthy of note. Controversies then existed with regard to the function of *Aspergillus oryzae* in Sake fermentation. It was thought, on the one hand, that the conidia (spores of the fungus) may transform, under certain favorable conditions, to peculiar yeast cells whose action induces the saccharified mash of rice to Sake, containing 10-15 per cent alcohol. Korshelt propounded this theory but was opposed by Atkinson. I, myself, confess that I shared the same view with Korshelt, but later was led to abandon it. Juhler, confirmed by Jorgenson<sup>3</sup> and Hansen,<sup>4</sup> also gave opinions agreeing with the transformation theory. Kozai and Yabe<sup>5</sup> showed that *Aspergillus* and *Saccharomycetis* have nothing in common. Klocker, Schioning, Seiter and Sorrel finally established the error of the transformation theory.

*Acclimatization of Aspergillus Oryzae*—For a few years I have been working on acclimatizing *Aspergillus oryzae* to various kinds of antiseptics. The art of acclimatizing fungi to antiseptics is not new, e. g., the growth of yeast in a medium containing fluoric acid or other antiseptics has been tried and also put into practice. Effront's attempt to increase fermentation products in the distillery by means of his process is well known. It consists of acclimatizing yeast to hydrofluoric or some other inorganic acid and then employing it in a mash containing the acids so that yeast can multiply without being disturbed by the various bacteria which gradually infect the mash. So far as I know, nobody has yet tried to acclimatize *Aspergillus oryzae* for practical purposes. This is because the utilization of this interesting fungus is very little known, or is ignored in the U. S. and Europe, while the use of antiseptics is rather unnecessary in the fermentation industry of the Orient, since it prefers mixed culture to the pure, on account of the flavor or bouquet of products still thought to be imparted from a mixed culture.

Since my object in producing the culture of *Aspergillus oryzae* is chiefly concerned with the utilization of its amyloclastic property developed during its growth and multiplication, it matters little whether the culture medium employed contains antiseptics

<sup>1</sup> Mittheilungen deutschen Gesellschaft für Natur und Völkerkunde Ostasiens zu Tokyo, Heft 16.

<sup>2</sup> "Wakrebericht der Schleisiochen Gesellschaft für Vaterl." Kultur, Bd. LXI (1883), p. 236.

<sup>3</sup> Centralblatt für Bakteriologie, II, Bd. I, pp. 16, 326.

<sup>4</sup> Loc. cit., p. 65.

<sup>5</sup> Centralblatt für Bakteriologie, II Abt., Bd. I, p. 619.

or not, provided I can get the culture which is possessed of maximum enzymic function. To the growth of *Aspergillus oryzae* on wheat bran as a culture medium I gave the convenient name of Taka-Koji and have employed it for a number of years to distinguish it from that known in Japan as Koji which is a culture on steamed rice.

Taka-Koji is designed for a substitute for malt as an amylolytic agent in varied fermentation and other allied industries. Its proposed use is encouraged by the fact that the cost of malt is subject to fluctuations according to the crop conditions of barley while bran is exempt from similar market conditions. Besides, the transformation of bran into Taka-Koji can be accomplished in 48 hours, while malting needs three or four times as long for completion of the process.

The making of Taka-Koji, as it was formerly practiced, was described by myself<sup>1</sup> some years ago, before the New York Section of the Society of Chemical Industry.<sup>1</sup> Later, several improvements were made and quite recently a radical departure was made in the mode of effecting the culture. I will, however, describe briefly the process as practiced some years ago, so as to facilitate my exposition of the subject matter.

The process consists of first moistening and then steaming wheat bran, so as to sterilize the material and at the same time to gelatinize the starch. After cooling the steamed mass down to 40° C. a small quantity of the spores of fungus are intimately mixed with it. It is now carried into a room where the floor is cemented, and spread in a thin layer of about 1½ inches thick. It is still better if put into a number of trays with wood or metal frames, and provided with a false bottom of wire netting, fine enough to hold the particles of bran. The layer can be made in this case a little thicker since air supply can be obtained from both top and bottom. Such trays are placed upon a specially constructed rack to hold the trays one above the other and about 2 inches apart. The temperature of the room is kept at about 30° C. at the beginning by means of opening steam jets direct into the space. This also keeps the room moist and warm. Within 16 to 18 hours the fungus commences to multiply, which action is easily followed by the gradual rise in temperature in the room. From this time on steam is turned off gradually and at last entirely shut off. After 20 to 24 hours from the time of inoculation the growth and multiplication of the fungus becomes so vigorous that it is necessary to cool the room by the introduction of fresh, cool air. Carbon dioxide resulting from the vigorous growth of the fungus becomes very conspicuous and the room needs the renovation of air which is effected by the air draft introduced for cooling purposes. Care should be taken that the air is supersaturated with moisture, so that the culture medium can always be kept from drying. The temperature of the room often goes up as high as 40–42° C. As long as the growth of fungus is comparatively pure and the mass is kept moderately moist to furnish the necessary amount of water for the culture, such a high temperature does not interfere with the genera-

tion of amylolytic enzyme in fungus cells and its secretion into the medium. The optimum temperature of the fungus growth lies, however, between 30–35° C. It is, of course, desirable to keep the temperature as nearly as possible between these limits. For 8 or 10 hours the multiplication of fungus is most vigorous and there high temperature prevails. Then a gradual decrease in temperature is noticed until the culture medium is replete with the mycelia of fungus within 48 hours from the time of inoculation. At this point vigorous and numerous conidiophores are already to be seen with yellow or greenish yellow conidia (spores). The diastatic strength of Taka-Koji has now reached its maximum and the Taka-Koji is ready to be taken out for use. When the vigorous growth of fungus has ceased the medium is liable to be easily infected with injurious bacteria which may destroy the diastase already generated. It is, therefore, necessary to conduct dry air into the room where Taka-Koji is manufactured, so that it shall be dried and made exempt from destructive infection. When the moisture of Taka-Koji is reduced to 10–15 per cent, it is immune from infection of bacteria and can be kept for several months. By use of antiseptics such as formaldehyde, benzoic or salicylic acid bacterial infection of Taka-Koji can be easily avoided.

While mould fungi in general can tolerate quite a quantity of antiseptics, nevertheless, if they are acclimated to same such toleration will attain to a conspicuous degree. One part of formaldehyde to 2500 parts of a culture medium does not considerably hinder the development of fungus. As to benzoic or salicylic acid, one part to 300 parts of a medium is almost immune to fungi. I had *Aspergillus oryzae* acclimated and the result of using it enabled me to obtain Taka-Koji 100 per cent stronger in amylolytic power than the product obtained by the old process.

#### DRUM EXPERIMENTS

Encouraged by this result, I thought of growing the acclimated fungus on the culture medium placed in a cylinder similar to a pneumatic malt drum. This is not a new idea. I carried out a series of experiments nearly twenty years ago, but then without the use of the acclimatized variety of *Aspergillus oryzae*. My experiments were then a total failure, which made me think the fungus could not grow on the material in motion. If we consider the case of sprouting barley in a pneumatic drum, it is, of course, seen that the development comes from within, where the vitality of the seed resides; hence the slight impediment, due to frictions between the moving mass, is not sufficiently severe to totally inhibit the sprouting of the grains. The case is different when the fungus is grown on the culture medium in motion, since it must develop and multiply where frictions must always be injuring delicate mycelial cells of fungus. In my early experiments, it was noticed that the fungus shows an initial growth indicated by the rise of temperature and also observed under the microscope, but it gradually retrogrades. Meanwhile, bacterial infection sets in and totally destroys the fungus growth.

<sup>1</sup> Journal of Applied Society of Chemical Industry, London, Feb. 28, 1898.



The subject once almost forgotten, returned to my mind as I said above, and I decided to repeat experiments again. A small experimental cylinder revolving a few times per minute was made out of a Mason jar and clock mechanism. About 30 grams of steamed bran were put in it and mixed with the new variety of acclimated fungus and the whole was kept in an enclosure maintained at 30° C. Unexpectedly a fair result was obtained in which I noticed a very interesting fact, namely, one side of the bran particle is covered with the fungus. It is the inner side of the bran. This side is coarse in structure and is rich in starch and protein matter. If the bran is moistened and steamed, this particular side shows a tendency to curl inward and assumes the shape of pericarp previous to its severing from the kernel. When each particle of the bran has curled, the inner side is naturally protected from the friction between particles when they are put in cylinders and motion is imparted to the mass by revolution.

My success and observations encouraged me to construct larger apparatus for 100 grams, 1 kilo, 5 kilos, 20 kilos and finally 70 kilos capacity. I was very glad to confirm in every experiment my belief that the process of making Taka-Koji in a pneumatic drum is feasible. Therefore, I ordered a drum of about 4800 pounds capacity for Taka-Koji manufacture, which is the size for an 8-ton malt drum. In this drum many new devices were introduced, but to my grief, such elaborate devices became in fact stumbling blocks and the experiments were far from successful. The new devices were taken out one after another until at last the drum remained as simple as that of my own laboratory make. At length, after repetitions of more than fifty experiments, I was enabled to obtain a fairly good outcome and was able to show that the process could be accomplished successfully on a large scale. The first drum became so dilapidated from the alterations and changes that I had to order the second apparatus. It is now ready and I am soon to try it out. Its success is hardly to be doubted.

The drum consists of a huge, plain iron cylinder provided with inlet on one side and outlet on the other, through which air can be passed by means of a suction fan located on the outlet side. The apparatus is furnished with mechanism to turn the cylinder at the rate of once per minute. An iron pipe runs through the center of the cylinder independent from it. It branches out in several places along the whole length, each branch ending in a spray nozzle, through which water or steam can be turned upon the material. The Koji manufacture in this drum is carried out as follows: The wheat bran is dumped in, then the necessary quantity of water and finally the steam is added, the mass being put in motion by revolution of the drum. As soon as the mass is properly steamed, it is cooled to 45° C. cool moist air. Into this mass an aqueous solution of antiseptics and then spores of the fungus suspended in water are sprayed. The temperature of the mass is generally at 38-40° C. The drum is now brought to a standstill and left for about 12 hours, when the gradually decreased temperature

again commences to go up. This means initial growth of the fungus. The drum is now put in motion and a slight air current is passed over the mass, care being taken that the temperature should not be lower than 30° C. At the eighteenth hour the temperature shows a tendency to rise quickly and at the twenty-fourth hour it reaches its maximum. The force of the air current is increased accordingly to keep the temperature at about 38° C. A suction pump of 1600 to 1800 cubic feet capacity per minute was put in full action yet the mass of 2400 pounds was barely within the limit of 38° C. According to my small experiment, a higher temperature of 42° C. did not impair the diastatic activity formed by the growth of the fungus; but if it is kept within 40° C. it is so much better for the process, that the air is previously cooled and saturated with moisture by drawing through a freely sprayed coke tower. In 48 hours the process is concluded.

The Taka-Koji manufactured in the drum is more compact and glossy than that grown otherwise. The inward side of the bran is covered with a felt-like growth of mycelia which do not branch out many conidiophores bearing spores; hence the color is whitish.

The labor needed for this process is reduced to one-sixth of that necessary in the old process. The saving of space is also considerable and the quality of Taka-Koji is excellent. Thus the process promises well for furnishing a substitute for malt in alcoholic fermentation and other industries, where amyloclastic enzyme is required.

Dr. Niels Ortvad, Chief Chemist of Hiram Walker & Sons, of Walkerville, Ontario, Canada, kindly carried out a series of experiments in his distillery and published his results in his paper contributed to the last Congress of Applied Chemistry, held here in New York. To quote briefly, he said:

"On account of the numerous great variations in the price of barley malt (in two consecutive years the price varied 100 per cent), it would be of great value to the distilling industry if a converting medium of moderate and more uniform price could be employed instead of barley malt. Eliminating, therefore, the different grains as a source of converting medium, I turned to the diastase produced by a microorganism, the *Aspergillus oryzae*. Takamine was the first to introduce the Koji process in America. As far back as 1889 he advocated the use of Koji in the distilling industry. Instead of growing the fungus on rice, Takamine employed a material far cheaper for this country, namely, wheat bran. An extract of the wheat bran, on which the *Aspergillus oryzae* had been allowed to germinate, contained the diastase, produced by the *Aspergillus*, and this extract was mixed with the mashed grain, bringing about the conversion of the starchy materials. Lately, I understand, he has succeeded in adapting a modification of the Galland-Henning malt drum system to his process. This should be a great improvement over the old floor system, in so far as it makes it possible to work under absolutely sterile conditions. For my experiments I decided to use the Taka-Koji itself instead of the

diastatic extraction of same and add it to the mash in the same way as malt. Before beginning the practical experiments in the distillery, laboratory experiments were conducted on a small scale to ascertain the amount of Taka-Koji which was necessary to convert a certain amount of starch into sugar, and also the optimum temperature at which to conduct the conversion. It was found that 4 g. of Taka-Koji was sufficient to give a complete conversion in a mash made from 96 g. of corn and rye, the corn containing 15.0 per cent of moisture and the rye 14.0 per cent. Three experiments were made in the distillery. For the first experiment only a 14 gallon can was used and a portion of our ordinary mash from the mashtub was employed, the mash being taken from the main mash just before malt was going to be added for conversion. The second experiment was performed on a somewhat larger scale. Instead of using mash material from the mashtub, the mash was made separately. It consisted of 500 kg. altogether, of which 20 kg. were Taka-Koji. The third experiment was performed on a good-sized working scale. Two mashes, each consisting of 3,401.94 kg. (of which 131.5 kg. were Taka-Koji), were prepared. The two mashes were filled in Turn No. 25 of Friday, May 26, 1911. Turn No. 25 was distilled separately and the yield was 36 liters of 100 per cent alcohol per 100 kg. of mash material, just a trifle higher than the yield of the other mashes which were made the same day. In judging the adaptability of Taka-Koji for use in distilleries several questions must be asked and answered:

"Is Taka-Koji capable of giving a complete conversion of the starchy materials in the mash?"

"Yes, 4 per cent of the air-dried Taka-Koji will in 15 to 20 minutes give a complete conversion of well prepared mash material.

"Is the fermentation a satisfactory one?"

"While it is accompanied by a strong odor, which is prevalent in the fermenting room, the fermentation, however, is very rapid and complete, and on this account should give rise to the least amount of infection.

"Is the yield of spirit satisfactory?"

"Yes, the yield obtained was a little higher than the yield gotten from the barley malt mashes, although the total fermentable extract available in the mash material was less. The yield of 36 liters of 100 per cent alcohol per 100 kg. of mash material is of course only a comparative yield. In distilleries which employ cookers and boil the corn under pressure, a higher yield would naturally result.

"Therefore, I should say as a final conclusion that in distilleries which make commercial or potable neutral spirit, the Taka-Koji process could be introduced to advantage. Aside from a probable higher yield in spirit, the saving in malt bill would be worth while in years with normal malt prices and very considerable in years when the malt prices become abnormal."

#### TAKA-DIASTASE

An aqueous extract from the Taka-Koji can be easily made by percolation and an enzyme can be precipitated by adding alcohol to such extent as to contain 70 per cent by volume of same in the mixture.

The precipitate is dehydrated by means of strong alcohol, dried and powdered. It is a white or yellowish white powder of hygroscopic nature. It is marketed in this form for medical use under the name Taka-Diastase.

Though known as an amylolytic agent, it contains various enzymes; nevertheless, amylolytic and proteolytic enzymes predominate. O. Kellner and his pupils early reported<sup>1</sup> the presence of invertase maltase beside amylase. Newcombe<sup>2</sup> established the presence of cytase, while Aso reports, in a Bulletin of the Agricultural College of Japan, the presence of orydate in Koji extract. According to Brunstein, Koji contains an emulsin-like substance that decomposes helicin into salicylic aldehyde and glucose which former is later oxidized into salicylic acid; amygdalin is decomposed into cyanhydrin and glucose, which former is later oxidized to mandelic acid.

Investigations on peptase and ereptase carried out by S. H. Vines<sup>3</sup> are replete with interesting observations. He found that Taka-Diastase contains the above enzymes and effected the separation of one from the other. By treating Taka-Diastase with 50 per cent ethyl alcohol and leaving it over 48 hours ereptase went into solution while peptase remained behind. Equally valuable and interesting are researches of J. Wohlgemuth.<sup>4</sup> He states that Taka-Diastase contained an enormous amylolytic function; the valuation of same according to his method showed to be  $D_{24}^{38} = 62,500$  ("D" Diastatic power digested at 38° C. for 24 hours). Testing tryptic action of Taka-Diastase he found that one gram corresponds to nearly 100 cc. of the pancreatic juice of man as well as dog; hence he recommended the use of Taka-Diastase for therapeutics in cases of general debility. Wohlgemuth also proved the presence of maltase, chimosin, ereptase, and lipase in Taka-Diastase.

Quite recently, Kita<sup>5</sup> reports the discovery of a specific enzyme in Taka-Diastase or in a Koji extract, whose function is to transform starch direct into glucose. He doubts very much the opinions entertained by preceding investigators that Taka-Diastase first transforms starch to maltose and that the latter is converted to glucose by the action of the maltase present. His experimental data have not yet been confirmed by any other experimenter. Such an enzyme as Kita reports probably exists but confirmation by more exhaustive proofs than he has furnished must be had.

The resistance of amylolytic enzyme of Taka-Diastase toward acid is reported by many investigators. This fact becomes very significant when applied to the practical conversion of grain mash. In a grain mash where 10 to 15 per cent sugar is to be finally produced an addition of mineral acid, say sulfuric acid, to an amount of 1 part to 2000 parts of mash accelerates the diastatic action at least 10 to 15 per cent. An equivalent of hydrochloric acid gives a

<sup>1</sup> *Zeitschrift für physiologische Chemie*, **14**, Part III.

<sup>2</sup> *Annals of Botany*, **13** (1889), No. 49.

<sup>3</sup> *Ibid.*, **24** (1910), No. 93.

<sup>4</sup> *Biochemische Zeitschrift*, **39**, Parts 3 and 4.

<sup>5</sup> *This Journal*, **5** (1913), 220.

similar result. Malt diastase is entirely inactive with such a high percentage of acid in mash.

Taka-Diastase possesses an important property as a medical agent; *i. e.*, it is more stable than the diastase of malt. The latter loses its activity gradually and within several months its activity dwindles, while Taka-Diastase remains almost unchanged for several years. How this stability is imparted to it is a subject full of interest for investigation. Taka-Diastase contains generally 10 to 15 per cent of ash; this can be reduced to 4 to 5 per cent by reprecipitations but the activity of the enzyme does not increase even by this apparent purifying process but on the contrary a loss of activity is occasioned in most cases.

The author extends his thanks to Mr. Wooyenaka for his untiring and valuable assistance and to Parke, Davis & Co., for affording every facility for carrying out the "Drum Experiments."

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### ALCOHOL IN THE MANUFACTURE OF PHOSPHORIC ACID AND PHOSPHATES

By PAUL J. FOX<sup>1</sup>

Received June 1, 1914

The increasing tendency in the fertilizer trade in this country to produce a concentrated complete fertilizer makes the question of the production of cheap phosphoric acid of special interest. Whatever process of separation is used, it is clear that the original source can be only the natural tri-phosphates of lime—phosphorites, apatite, and the rock and pebble phosphate of the sedimentary beds.<sup>2</sup>

For the separation of the phosphoric acid, a large number of methods have been patented. It is not the writer's intention to review or even enumerate these methods. He desires merely to make a suggestion.

It is difficult to see, when the energy relations are considered, how anything cheaper can be found than sulfuric acid as the prime separator of phosphoric acid from calcium phosphate. When we consider that sulfuric acid is in part formed by the combustion of a substance very common in nature and very cheaply obtained, and moreover is a product which must be manufactured in some cases to avoid damage to vegetation, it is clear that with the progress of chemical technology, we may expect the present price of about four dollars and a half per ton to go down rather than up.

In view of these considerations, it appears that the cheapening of the production of relatively pure phosphoric acid is rather a question of extraction than of some other method of setting free the phosphoric acid from phosphate rock. The writer suggests the use of denatured alcohol for this purpose. The plan would be to treat the phosphate rock with the theoretical amount of sulfuric acid of about 50° Baumé, taking care to bring about thorough incorporation

of the acid and consequent decomposition of the rock, by mechanical mixing. The mixed mass of phosphate rock and sulfuric acid is then leached with denatured alcohol, the residue being filter-pressed. This yields a pure alcoholic solution of phosphoric acid, the sulfates, undecomposed phosphates, etc., being left behind.<sup>1</sup>

The most favorable strength of alcohol, whether 95 per cent or more dilute, to be used in the process, would have to be determined under factory conditions, and would depend on the subsequent treatment adopted. The same remark applies to the sulfuric acid.

The method involves nothing new in theory, but so far as the writer knows has no application on an industrial scale. Besides the obvious advantage of yielding a phosphoric acid substantially free from calcium, the plan offers the following further features: If it is desired to evaporate the extract to produce pure phosphoric acid, the specific heat of alcohol is only 0.5452 to that of water as unity. The boiling point of alcohol is 78.4° as against 100° for water. The latent heat of vaporization of alcohol is 206.4° (at 78° C., Schall) as against 536 (at 100° C.) for water. The figures for specific heats and latent heat of vaporization refer, of course, to unit weight. When we consider unit volume, we see that the thermal capacity of a given volume of alcohol is (taking density of alcohol at 20° = 0.789) only 0.430 to water as unity, and the latent heat of vaporization similarly computed is 0.304 to water as unity.

Another phase of the question is of interest. In case it is desired not to separate the phosphoric acid, but to prepare immediately a concentrated fertilizer of saline character, many double decompositions and precipitations can take place in alcoholic solution which are impossible in aqueous solution except at a great concentration. For example, various potassium and ammonium phosphates may be more easily precipitated in alcoholic solution than in aqueous.

In particular various phosphates can be precipitated by merely adding aqueous ammonia, in slight excess, to an alcoholic solution of potassium chloride and phosphoric acid; or better by conducting in gaseous ammonia. The double decomposition depends on the solubility of potassium chloride in alcohol of various concentrations and the insolubility of potassium and other phosphates in that medium. Again, by merely digesting solid potassium chloride with alcoholic phosphoric acid, potassium phosphate results, though the progress of the double decomposition is limited by the hydrochloric acid set free. The progress of the double decomposition may be followed in a roughly quantitative manner with a microscope provided with Nicol prisms, as the potassium chloride is isotropic and the potassium phosphate anisotropic. If the hydrochloric acid thus set free, however, is neutralized by aqueous or gaseous ammonia, ammonium phosphate and potassium phosphate are precipitated, certainly as a mixture of two or more salts and possibly in part as

<sup>1</sup> Dr. Cameron has suggested that a plan might be worked out whereby the phosphate rock would be treated in one process with a mixture of alcohol and sulfuric acid.

<sup>2</sup> Scientist in Physical and Chemical Investigations, Bureau of Soils.

<sup>1</sup> It is not meant to imply that there is any such definite chemical compound as calcium tri-phosphate. The material of approximately this composition is probably a solid solution. See Cameron and Seidell, *Jour. Am. Chem. Soc.*, **27** (1905), 1503; and Cameron and Bell, *Ibid.*, p. 1512. Apatite always contains chlorine or fluorine. See Cameron and McCaughey, *Jour. Phys. Chem.*, [5] **15** (1911), 463.



a double salt. In any case it appears to be necessary to work in acid solution in order to prepare a stable salt, or mixture of salts, of the fertilizer constituents. The correct strength of alcohol and many other details would have to be worked out.

Another interesting feature is the per cent of water in the alcohol distilled off. Does the calcium sulfate form hydrate itself at the expense of the water in dilute alcohol? The answer to this question would depend on the range of existence of calcium sulfate di-hydrate in contact with alcohol of various concentrations, at the temperature worked with; also on the vapor pressure of mixtures of phosphoric acid and alcohol. It is, of course, presumed that the original calcium phosphate is nearly dry, or at least contains no more water than can be absorbed by the sulfuric acid used. The points involved would require a good deal more investigation than the writer has time for. A laboratory trial showed that the resulting calcium sulfate was not hydrated to the extent of two molecules of water to one of calcium sulfate. Though calcium sulfate is so abundant in nature, especially in the arid regions of the far west, as to have slight value, it is extensively used for plaster and other purposes, and is mined in convenient places. It is possible that the extremely fine grain of the calcium sulfate resulting from the production of phosphoric acid, together with the accessible places at which it would be prepared, would give it some commercial value.

To the advantages set forth may be added the fact that the alcoholic solutions are easy to filter and less corroding on the filters than aqueous phosphoric acid. Of course there would be some loss of alcohol which would escape recovery. But with the advance of chemical technology, it is believed that these losses can be minimized. Evaporators designed for removing volatile solvents are becoming very common. Alcohol is tending to become cheaper rather than dearer. Especially if the manufacture of plaster is combined with that of phosphoric acid, the problem would be simple, as the heating of the residue to bring it to the right state of hydration would, at the same time, make recovery of the alcohol possible. As a last resort, the fuel value of the alcohol might be utilized by drawing the draft for the boiler fires over it, with appropriate devices to prevent back firing or ignition of the possibly explosive mixture of air and alcohol vapor.

As a denaturing agent for the alcohol, pyridin would probably serve best, as only an exceedingly small per cent (which would, in no way, interfere with the reactions) is necessary to give the alcohol such an odor as effectually to prevent the consumption of it for any purpose other than that intended.

All the foregoing is intended to be merely in the nature of suggestion. To work out all the problems involved, physical-chemical and technical, would require much time, and in so far as the technical features are concerned, special facilities. However, to test the ease of extraction of the phosphoric acid by alcohol, two experiments were made, each on one hundred

grams of calcium phosphate. The material used had the following composition:

	Per cent
P <sub>2</sub> O <sub>5</sub> . . . . .	37.6
CaO . . . . .	42.2
Water . . . . .	14.5
Undetermined (by difference) . . . . .	5.7
	100.0

EXPERIMENT I—The one hundred grams of phosphate (after being treated with the sulfuric acid of 50° Baumé) were extracted with 95 per cent alcohol, using a large Buchner funnel. After drying in a vacuum over sulfuric acid, the residue amounted to 105.5 grams and contained 0.3 of one per cent of P<sub>2</sub>O<sub>5</sub>, amounting to an extraction of 99.2 per cent of the P<sub>2</sub>O<sub>5</sub>.

EXPERIMENT II was the same except that 50 per cent alcohol was used for the extraction. The residue was 106.0 grams and contained 0.6 per cent P<sub>2</sub>O<sub>5</sub>, giving an extraction of 98.7 per cent.

No particular significance is to be attached to these small differences in extraction, except possibly that the stronger alcohol as it penetrates the mass with extreme readiness, extracts the phosphoric acid a little more thoroughly. With the strong alcohol especially, the extraction works with great ease and rapidity and from this point of view at least, the use of strong alcohol is advantageous.

BUREAU OF SOILS, WASHINGTON

## THE ACTION BETWEEN CLAY FILTERS AND CERTAIN SALT SOLUTIONS<sup>1</sup>

By W. B. Hicks

Received June 5, 1914

Colloidal suspensions such as are obtained when soils and clays are extracted with water pass readily through the best grades of filter paper, but yield perfectly clear filtrates when filtered through Pasteur-Chamberland or other close-grained porcelain filters. In many cases, however, this treatment changes the composition of the solution. Briggs<sup>2</sup> has shown by titrating the chlorine that no change in concentration occurs when *N*/1000 solutions of sodium chloride are passed through clay filters. By titrating the alkalinity the same investigator observed no change in *N*/20 sodium carbonate and bicarbonate solutions, a decrease of 2 per cent in *N*/100, and a diminution of 15 per cent in *N*/1000 sodium carbonate solutions. By conductivity measurements he found a slight decrease in concentration in the first 50 cc. fraction on filtering *N*/1000 solutions of a number of salts. Sullivan<sup>3</sup> observed that clay filters absorb about 18 per cent of the iron from *N*/1000 ferric sulfate solutions without absorbing any of the SO<sub>4</sub> radicle. He noted that other bases go into solution, but in quantities insufficient to account for the iron absorbed.

The results of these investigators show that clay filters retain very little or none of the acid radicle, but may retain considerable quantities of the base when salt solutions are passed through them. However, it was thought necessary to repeat some of Briggs' work in order to determine whether such filters are

<sup>1</sup> Published by permission of the Director of the U. S. Geological Survey.

<sup>2</sup> U. S. Dept. Agr., Bur. Soils, Bull. 19, 1902.

<sup>3</sup> Econ. Geol., 3 (1908), 754.

uniform in their behavior during filtration. At the same time a more extended investigation of the subject was considered desirable. It seemed important to know the composition of the filters, how much they are dissolved by salt solutions and to what extent they become "salted" and thereby contaminate a succeeding solution filtered through them. Answering these questions experimentally and thus obtaining a more definite idea concerning the action between clay filters and salt solutions led to the experimental results here presented.

In the experiments ordinary 8 in. Pasteur-Chamberland water filters were used. These showed on analysis the following percentage composition:

SiO <sub>2</sub> .....	58.70	CaO .....	0.39	Na <sub>2</sub> O .....	0.40
Al <sub>2</sub> O <sub>3</sub> .....	39.20	MgO .....	0.18	K <sub>2</sub> O .....	1.54
Total .....	100.41				

The filters were fitted with 200 cc. glass containers and ordinary side neck filter flasks. They were cleaned by washing in turn with water, concentrated hydrochloric acid, and then with water until the last washings showed only a slight opalescence with silver nitrate.

TABLE I ACTION OF PORCELAIN CLAY FILTERS ON PURE SALT SOLUTIONS

SOLUTION	Cc. filtered	Cc. taken for analysis	RESIDUE Grams	Change in concentration Per cent	Grams Cl by titration	Change in Cl Per cent	SiO <sub>2</sub> Gram	Alkalinity Cc. N/10 HCl required	Change in alkalinity Per cent
<i>N/10 Na<sub>2</sub>SO<sub>4</sub>—Original.....</i>	...	25	0.1777 (a)	...	...	...	...	...	...
Filtrate from Filter 1.....	400	25	0.1773	-0.23	...	...	...	...	...
Filtrate from Filter 2.....	400	25	0.1775	-0.12	...	...	...	...	...
<i>N/10 K<sub>2</sub>SO<sub>4</sub>—Original.....</i>	...	25	0.2175	...	...	...	...	...	...
Filtrate from Filter 1.....	400	25	0.2171	-0.18	...	...	...	...	...
Filtrate from Filter 2.....	400	25	0.2171	-0.18	...	...	...	...	...
<i>N/9.84 Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>—Original.....</i>	...	25	25.40 (b)	...	...	...	...	...	...
Filtrate from Filter 1.....	400	25	25.40	...	...	...	...	...	...
Filtrate from Filter 2.....	400	25	25.45	...	...	...	...	...	...
<i>N/10 NaCl—Original.....</i>	...	25	0.1457 (c)	...	0.0886	...	...	...	...
Filtrate from Filter 1.....	400	25	0.1453	-0.27	0.0882	-0.45	0.0012	25.00	-0.30
Filtrate from Filter 2.....	400	25	0.1453	-0.27	0.0882	-0.45	0.0013	24.95	-0.20
<i>N/10 KCl—Original.....</i>	...	25	0.1864	...	0.0887	...	...	...	...
Filtrate from Filter 1.....	400	25	0.1859	-0.27	0.0885	-0.23	0.0007	24.10	-0.41
Filtrate from Filter 2.....	400	25	0.1860	-0.22	0.0886	-0.12	0.0009	24.08	-0.50
<i>N/100 KCl—Original.....</i>	...	100	0.0746	...	0.0355	...	...	...	...
Filtrate from Filter 1.....	400	100	0.0742	-0.54	0.0353	0.57	...	...	...
Filtrate from Filter 2.....	400	100	0.0742	-0.54	0.0355	-0.00	...	...	...
<i>N/7.85 CaCl<sub>2</sub>—Original.....</i>	...	25	0.2179 (d)	...	0.1128	...	...	...	...
Filtrate from Filter 1.....	400	25	0.2177	-0.09	0.1124	0.35	0.0017	4.84	...
Filtrate from Filter 2.....	400	25	0.2177	-0.09	0.1124	0.35	0.0017	4.35	-10.12
<i>N/10 Na<sub>2</sub>CO<sub>3</sub>—Original.....</i>	...	25	0.1460 (e)	...	...	...	...	...	...
Filtrate from Filter 1.....	400	25	0.1469	+0.62	...	...	0.0012	24.95	-0.30
Filtrate from Filter 2.....	400	25	0.1471	+0.68	...	...	0.0013	24.95	-0.20
<i>N/10.33 K<sub>2</sub>CO<sub>3</sub>—Original.....</i>	...	25	0.1805	...	...	...	...	...	...
Filtrate from Filter 1.....	400	25	0.1809	+0.22	...	...	0.0007	24.10	-0.41
Filtrate from Filter 2.....	400	25	0.1810	+0.28	...	...	0.0009	24.08	-0.50
<i>N/10.33 K<sub>2</sub>CO<sub>3</sub>—Original.....</i>	...	500	0.0361	...	...	...	...	...	...
Filtrate from Filter 1.....	800	500	0.0387	+7.20	...	...	0.0017	4.35	-10.12
Filtrate from Filter 2.....	800	500	0.0397	+9.97	...	...	0.0017	4.50	-7.30

(a) On evaporation and ignition.

(b) Titration with N/10 NaOH and Mannitol-Cc.

(c) On evaporation and gentle ignition

(d) As sulfate.

(e) On evaporation as chloride

To obtain a measure of the solvent action of water on these filters, 300 cc. of distilled water after passing through them were evaporated, ignited and weighed. The results from each of two filters gave 0.0013 g. or 0.0004 g. per 100 cc. This was repeated, after passing 2000 cc. of water through each filter, with a residue of 0.0003 and 0.0002 g. per 100 cc. The evaporation of 250 cc. of distilled water left a residue of 0.0002 g. per 100 cc. It is thus seen from these results that the solvent action of water on these filters is very small.

In order to determine what changes take place in a solution on passing through clay filters, two series of experiments were carried out:

I—Pure salt solutions of known composition were allowed to pass through the filters and the resulting change in concentration determined by analyzing the filtrates.

II—The quantity of base retained by a filter when a salt solution is allowed to pass through it was determined directly by extracting the base with a different salt solution and analyzing the extract.

The first series of experiments was carried out by washing the filters with water until the washings were free from salts, sucking air through them to remove as much water as possible, passing the particular salt solution under investigation through the filter, discarding the first 50 cc., and analyzing the filtrate. The solutions were prepared from Baker's analyzed chemicals, and were analyzed in the same manner as the filtrates. The results are given in Table I.

On studying these results it will be observed that filtration through porcelain clay filters produces no change in the boric acid content in N/10 borate solutions and only very slight changes—roughly a loss of 0.2 per cent—in N/10 sulfate solutions of the alkalis. With chloride solutions, the loss in concentration is slightly greater, amounting to about 0.3 per cent in N/10 and 0.5 per cent in N/100 solutions. It will be further noted that the percentage loss in chlorine corresponds to that of the total solids, indicating that both ions of the salt in question are retained by the filter.

However, we must consider the fact that the magnitude of the changes with which we are dealing is quite small, and therefore the apparent changes may be due, in part, at least, to errors in analytical operations. At the same time the fact that all the sulfate and chloride solutions examined show a distinct loss in concentration, points out clearly that the filters do retain a portion of these salts. No calcium, aluminum, or silica could be found in the filtrates, indicating that these solutions have very little solvent action on the filters. With carbonate solutions of the alkalis, as the chemical data show, the results are somewhat different. There is an actual increase in total solids determined as chlorides amounting roughly to 0.5 per cent in N/10 solutions, and 8 per cent in N/1000 solutions. Silica was extracted from the filter in quantities almost equivalent to this gain. Calcium was also found in the extract. The alkalinity determined by titration with N/10 hydrochloric acid and methyl orange showed a slight diminution in N/10 solutions, and about 8 per cent decrease in N/1000 solutions. This loss in al-

kalinity indicates a direct absorption of the salt or of free base.

In the second series of experiments it was attempted to make a direct determination of the quantity of salts retained by porcelain clay filters.

In this case the filters were washed with a large excess of the salt solution under investigation to make sure that the maximum absorption had taken place, and then with distilled water until the washings were free from the salt in question. This treatment presumably left the filters still containing only the quantity of salt held so tenaciously that water would not remove it or at most would remove it very slowly. In the case of chlorides the filters were washed until only a slight opalescence was shown with silver nitrate in 200 cc. of the filtrate; with carbonates, until no alkalinity could be detected. This required from 2400 cc. to 4000 cc. of water, depending on the character and concentration of the solution. The salt which was still retained was then washed out by 100 cc. portions of a solution of  $N/5$  ammonium chloride, until a negligible or constant residue was obtained on evaporation and ignition. The various fractions were then analyzed with the results given in Table II.

TABLE II—SALTS EXTRACTED FROM FILTERS BY 100 CC. PORTIONS OF  $N/5$   $NH_4Cl$  AFTER PRIOR TREATMENT WITH

A—400 CC. 2 PER CENT KCl AND THOROUGH WASHING WITH WATER

	Filter No.	Residue (a) Gram	Combined filtrates		Grams K Calculated
			Grams KCl	Grams K	
(200 cc. Water).....	1	0.0010			{ 0.0002
	2	0.0011	0.0007	0.0004	{ 0.0002
Fraction I.....	1	0.0055			{ 0.0008
	2	0.0056	0.0031	0.0015	{ 0.0008
Fraction II.....	1	0.0020			{ 0.0003
	2	0.0025	0.0009	0.0005	{ 0.0003
Fraction III.....	1	0.0014			{ 0.0003
	2	0.0014	0.0011	0.0006	{ 0.0003
Fraction IV.....	1	0.0016			{ 0.0002
	2	0.0017	0.0008	0.0004	{ 0.0002

B—1000 CC.  $N/100$  KCl AND THOROUGH WASHING WITH WATER

(200 cc. Water).....	3	0.0031	0.0005	0.0003	{ 0.0002
	4	0.0026			{ 0.0002
Fraction I.....	3	0.0095	0.0035	0.0018	{ 0.0009
	4	0.0095			{ 0.0009
Fraction II.....	3	0.0025	0.0009	0.0005	{ 0.0003
	4	0.0026			{ 0.0003
Fraction III.....	3	0.0014	0.0006	0.0004	{ 0.0002
	4	0.0019			{ 0.0002
Fraction IV.....	3	0.0019	0.0006	0.0004	{ 0.0002
	4	0.0018			{ 0.0002

C—400 CC.  $N/10$   $K_2CO_3$  AND THOROUGH WASHING WITH WATER

Fraction I.....	1	0.0070	0.0033	0.0017	{ 0.0009
	2	0.0064			{ 0.0009
Fraction II.....	1	0.0017	0.0009	0.0004	{ 0.0002
	2	0.0017			{ 0.0002
Fraction III.....	1	0.0018	0.0006	0.0003	{ 0.0002
	2	0.0019			{ 0.0002
Fraction IV.....	1	0.0017	0.0006	0.0003	{ 0.0002
	2	0.0017			{ 0.0002

(a) All residues evaporated and weighed as chlorides.

The ammonia similarly retained by the filters from solutions of ammonium chloride was removed by washing with 200 cc. of a 2 per cent potassium chloride solution, the filtrate being caught in dilute hydrochloric acid. The ammonia was determined in the filtrate by the areometric method after evaporation to small bulk. To make sure that accurate results in the estimation of ammonia were obtained in this way, several determinations on known samples were made, with a recovery of 99.5 to 100.5 per cent. The results are given in Table III.

As these results show, a small but appreciable quantity of potassium is persistently retained by the filters even after long washing with water. This is largely but not completely removed by extraction with 100 cc.

of  $N/5$  ammonium chloride, a small and uniform quantity being extracted by succeeding fractions. Determined in this way, practically the same quantities of potassium are retained by the filters from all the solutions tested, indicating that the amount retained is independent of the concentration and character of the solution and possibly dependent only on the filters themselves. Moreover, the ammonia similarly retained from ammonium salts corresponds closely to that found

TABLE III—AMMONIA EXTRACTED FROM THE FILTERS BY 2 PER CENT KCl AFTER PRIOR TREATMENT WITH 400 CC. OF  $N/5$   $NH_4Cl$  AND THOROUGH WASHING WITH WATER

Cc. 2 per cent KCl solution used	Filter No.	Cc. for titration $N/10$ equivalent	$NH_3$ Gram
200	2	0.37	0.0007
200	3	0.37	0.0007
200	4	0.42	0.0008

for potassium salts. It thus appears that the filters become "salted" to a small degree and contaminate a succeeding solution filtered through them. At the same time the total residue extracted by ammonium chloride is much greater than the potassium content even when considered as the oxide or chloride, indicating that ammonium chloride exerts an appreciable solvent action on the filters.

In conclusion it may be pointed out that filtration through porcelain clay filters of the size here employed produces little or no change in the boric acid content from borate solutions, a slight decrease in concentration in sulfate and chloride solutions of the alkalies, a larger decrease in  $N/10$  carbonate, and a considerable decrease in  $N/1000$  carbonate solutions. It may be observed further that the filters become "salted" to a slight degree during filtration, and also that they are appreciably dissolved by solutions of ammonium chloride. Therefore, it may be said that the application of these filters depends on the character and concentration of the solution to be filtered. For moderately concentrated solutions and even for very dilute solutions of the chlorides and sulfates of the alkalies the percentage change, as a rule, is very small. By discarding the first portion, say 100 cc., of the filtrate, the liability of introducing a significant error can be much diminished.

U. S. GEOLOGICAL SURVEY  
WASHINGTON

## SELECTIVE ADSORPTION

By E. G. PARKER

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Adsorption, or sorption—a term recently proposed—is most satisfactorily explained at present as a concentrating of a solute at a surface, whether this concentrating effect is due to differences in surface tension or electrical potential. This adsorption of solute from solution follows certain arbitrary laws, a new constant being required according to the substance used, which furnishes the surface, the character of the surfaces of two different substances being apparently never the same. That certain surfaces not only have the power of adsorbing a solute as a whole from solution, but also have the power of absorbing a part of the solute at a greater rate than the other, or of selectively adsorbing, can be shown qualitatively in numerous ways. In case of the selective adsorption of one ion of an electrolyte an accompanying or previous



hydrolysis of the electrolyte is necessary, and the use of some of our common acid-alkali indicators is valuable in observing this phenomenon.

A silver nitrate solution shaken with animal charcoal and the supernatant filtered off and tested with methyl orange or litmus gives a distinct acid test.

A potassium chloride or nitrate solution shaken with cane sugar charcoal and the supernatant liquid tested with phenolphthalein gives the strong red color of alkaline reaction.

An interesting case of selective adsorption is to be found with Congo red and absorbent cotton. If the base of a column of absorbent cotton is immersed in a solution of Congo red made very slightly acid, in a very few minutes the cotton immediately above the solution is colored blue (acid reaction), while above the blue color for about an inch is seen the red color of neutral or alkaline reaction. Above the red the cotton is wet with water.

Innumerable other cases of selective adsorption in a qualitative way might be given. The object of this work is to attempt to show that in certain cases selective adsorption is quantitative as well as qualitative.

When a solution of a neutral salt is brought in contact with a soil a loss in the amount of the cation is obtained. The bases of the soil (Ca, Mg, etc.) are found in the resulting solution in amounts a little less than equivalent to the loss in that of the cation. The resulting solution is acid to common indicators. The loss of the anion in the solution is generally not appreciable. The amount of loss of the cation, of bases found in the resulting solution and the acidity of the resulting solution differ widely with the salt used. Methods of determining soil acidity by shaking a soil with a neutral salt solution are therefore useless as almost any desired acidity within limits might be obtained by selecting the right salt. These are not recent observations but have been explained contradictorily from time to time by various authors.

The absorptive properties of soils have been under investigation in this laboratory for several years under the direction of Dr. Frank K. Cameron, and several publications describing this work have appeared from time to time.<sup>1</sup>

On treating kaolin with solution of magnesium and sodium chlorides, Köhler<sup>2</sup> found the resulting solution to be slightly but distinctly acid to litmus, and attributed this to the fact that a selective concentration of the dissolved substance—an adsorption of the base—had taken place.

E. C. Sullivan<sup>3</sup> repeated these experiments and ob-

<sup>1</sup> Cameron, F. K., and Bell, J. M., "The Mineral Constituents of the Soil Solution," U. S. Dept. Agr., Bur. Soils, *Bull.* **30**, 1905; Cameron, F. K., and Patten, H. E., "The Distribution of Solute between Water and Soil," *Jour. Phys. Chem.* **2** (1907), 581-593; Patten, H. E., "Some Surface Factors Affecting Distribution," *Trans. Amer. Electrochem. Soc.* **10** (1906), 67-74; Patten, H. E., and Gallagher, F. E., "Absorption of Vapors and Gases by Soils," U. S. Dept. Agr., Bur. Soils, *Bull.* **51**, 1908; Patten, H. E., and Waggaman, W. H., "Absorption by Soils," U. S. Dept. Agr., Bur. Soils, *Bull.* **52**, 1908; Schreiner, Ostwald, and Failyer, G. H., "The Absorption of Phosphates and Potassium by Soils," U. S. Dept. Agr., Bur. Soils, *Bull.* **32**, 1906.

<sup>2</sup> Köhler, Ernst, "Adsorptionsprozesse als Faktoren der Lagerstättenbildung und Lithogenese," *Ztschr. Prakt. Geol., Jahrg.*, **11** (1903), 49-59.

<sup>3</sup> Sullivan, E. C., "The Interaction between Minerals and Water Solutions," U. S. Geol. Survey, *Bull.* **312**.

tained the same result, accounting for it by an exchange of the sodium and magnesium of these salts in part for the iron and aluminum of the kaolin, the salts of the latter undergoing extensive hydrolysis in dilute solution.

Van Bemmelen<sup>1</sup> treated 100 grams of soil with 200 cc. portions of solutions containing 8 and 40 milligram equivalents of potassium chloride. After filtration the solutions were analyzed, and it was found that an almost complete change of potassium for sodium, calcium and magnesium had taken place. Chlorine was determined in one experiment and had not changed.

Sullivan<sup>2</sup> found that by treating kaolin and various other silicates with salt solutions a quantity of bases almost equivalent to the loss of the base from the salt was dissolved in each case.

Wiegner<sup>3</sup> found that on treating an artificial, amorphous, water-containing (hydrated), so-called double silicate with a neutral salt solution the cation of the neutral salt was taken in part from the solution, and in its place the cations of the silicate-gel in nearly equivalent amounts entered the solution. The anion of the neutral salt remained unchanged, provided secondary reaction did not take place.

The soil, when brought in contact with a solution, presents a comparatively large surface, the nature of the surface being apparently such that the base of an electrolyte is adsorbed at a greater rate than the acid, since the resulting solutions are generally acid to indicators. By using a potassium salt solution (for example) and a soil, and assuming all the potassium removed from the solution to be adsorbed, the acidity of the solution will vary according to the amount of acid used up at equilibrium in a secondary reaction of the acid with the constituents of the soil. The amount of bases of the soil found in the resulting solution will be equivalent to the acid used up in this secondary reaction. The amount of anion adsorbed by a soil in the large number of cases is practically negligible. That these assumptions are correct is indicated by the following experimental data: 500 g. portions of a Durham sandy loam were shaken with 200 cc. of a solution of potassium chloride, of potassium acetate, and of water, at frequent intervals for two days. The soil was allowed to settle. Portions of the clear supernatant liquid were then pipetted off, filtered and analyzed. The supernatant liquid from the soil, shaken with pure distilled water, showed no appreciable presence of material dissolved from the soil, while analyses of the supernatant liquid from soil shaken with the above solution showed soil material present. The potassium chloride equivalents of the various constituents determined by these analyses are given in Table I.

In the foregoing experiments the determination of the free acid is unreliable, considering the fact that no indicator could be used for titrating, which was sensitive enough and at the same time unaffected by carbonate.

<sup>1</sup> Van Bemmelen, J. M., "Das Absorptionsvermögen der Ackererde," *Landw. Vers. Stat.*, **21** (1877), 135-191.

<sup>2</sup> Sullivan, E. C., *Op. cit.*

<sup>3</sup> Wiegner, Georg., "Zum Basenaustausch in der Ackererde," *Journ. Landw.*, **60** (1912): 111-150, 197-222.

bon dioxide. The results can be considered only as approximations. Boiling to remove the carbon dioxide is impossible when potassium acetate is used, since it hydrolyzes on boiling, giving an alkaline reaction to indicators. Iron and titanium were determined in several cases and found to be present in negligible amounts in the precipitated alumina.

From the data obtained, when the potassium chloride is used, the amount of potassium chloride equivalent to loss of potassium ( $0.7650 - 0.6950 = 0.0700$  g. per 100 cc.) during contact is greater than the amount of potassium chloride equivalent to the bases dissolved from the soil ( $0.0107 + 0.0353 + 0.0157 = 0.0617$

TABLE I—ADSORPTION BY DURHAM SANDY LOAM OF POTASSIUM FROM SOLUTIONS OF POTASSIUM SALTS  
Results stated in grams of potassium chloride per 100 cc. equivalent to constituents determined by analyses

Constituents by analysis	From Potassium Chloride Solution		Constituents by analysis	From Potassium Chloride Solution	
	Gram	Gram		Gram	Gram
K before contact	0.7650	0.7470	Mg after contact	0.0157	0.0167
K after contact	0.6950	0.6560	Na after contact		
Al after contact	0.0107	0.0015	Free acid after contact	0.0112	0.0402
Ca after contact	0.0353	0.0314	Anions after contact	0.7647	0.7450

g. per 100 cc.) by an amount ( $0.0700 - 0.0617 = 0.0083$  g. per 100 cc.) about equal to the amount of potassium chloride equivalent to the estimated free acid ( $0.0112$  g. per 100 cc.). When potassium acetate is used, the amount of potassium chloride equivalent to the loss of potassium ( $0.7470 - 0.6560 = 0.0910$  g. per 100 cc.) during contact is again greater than the amount of potassium chloride equivalent to the bases dissolved from the soil ( $0.0015 + 0.0314 + 0.0167 = 0.0496$  g. per 100 cc.) by an amount ( $0.0910 - 0.0496 = 0.0414$  g. per 100 cc.) about equal to the amount of potassium chloride equivalent to the estimated free acid ( $0.0402$  g. per 100 cc.).

When potassium acetate is used, the bases dissolved from the soil are 54.5 per cent [ $(0.0496 \div 0.0910) \times 100$ ] of what they would be if a complete exchange of bases had taken place, while, when potassium chloride is used, this percentage is 88.1 per cent [ $(0.0616 \div 0.0700) \times 100$ ].

If now this secondary reaction between the soil and the free acid present, due to the adsorption of potassium by the soil, be prevented by the addition of a small amount of sodium hydroxide to the solution, it having been previously determined that sodium hydroxide is not appreciably adsorbed by the soil, it is found that bases of the soil are not present in the resulting solution in appreciable amounts. A loss of potassium is obtained of about the same magnitude as in the previous case when the acid is not neutralized, and is allowed to react with the soil. A solution containing 18.38 g. of potassium chloride and about 1 g. of sodium hydroxide per liter in contact with a soil lost an amount of potassium equivalent to 0.1520 g. per 100 cc. of potassium chloride. The chlorine concentration remains unchanged. If too great an excess of sodium hydroxide, over that theoretically required to neutralize the acid present, is added, the resulting solution is discolored and iron in appreciable amounts is found to be present.

Believing, from the above and previous observations, that the loss of potassium from a solution of

a potassium salt in contact with a soil is due entirely to a selective adsorption of potassium, the hope of finding the effect of concentration, of size of soil particles, of nature of surface, and of presence of other substances on this selective adsorption of potassium led to the following experimental work.

#### EFFECT OF CONCENTRATION

Thirty-five gram portions of a Norfolk sandy loam and a Marshall silt loam were placed in 200 cc. bottles with solutions of potassium chloride, containing varying amounts of potassium chloride and a small amount of sodium hydroxide. The bottles were then rotated in a thermostat at room temperature for two days, and the resulting solutions analyzed. The results of the analyses are given in Table II.

TABLE II—EFFECT OF CONCENTRATION ON ADSORPTION OF POTASSIUM FROM SOLUTIONS OF POTASSIUM CHLORIDE BY NORFOLK SANDY LOAM AND BY MARSHALL SILT LOAM

	KCl equivalent to the K per 100 cc. of solution		Loss	
	Before contact Grams	After contact Grams	Per 100 cc. of solution Gram	Per cent
NORFOLK SANDY LOAM				
23.8550	25.6750		0.1800	0.70
14.7700	14.6500		0.1200	0.81
9.1250	8.9650		0.1600	1.75
6.2580	6.1100		0.1480	2.36
4.7400	4.5950		0.1450	3.06
3.1120	2.9600		0.1520	4.89
1.8380	1.7010		0.1370	7.45
0.6406	0.5640		0.0766	11.96
0.3064	0.2650		0.0414	13.51
0.1283	0.0960		0.0323	25.18
MARSHALL SILT LOAM				
11.8400	11.3500		0.4900	4.14
10.0450	9.5700		0.4750	4.73
6.6950	6.2450		0.4500	6.72
4.4860	4.0420		0.4440	9.90
2.6700	2.2400		0.4300	16.11
1.1640	0.7700		0.3940	33.81

From the results of this experiment (see Fig. 1) we find that from zero concentration of potassium chloride, where necessarily the adsorption of potassium is zero, the loss of potassium during contact increases

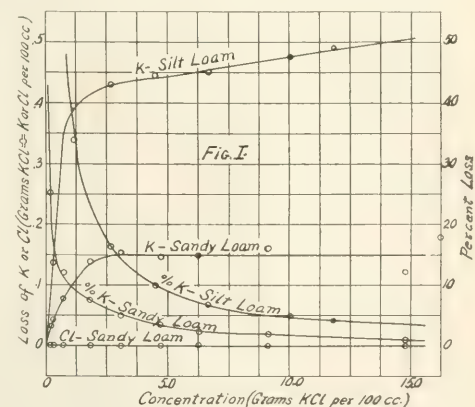


FIG. 1—CURVES SHOWING THE EFFECT OF CONCENTRATION ON THE SELECTIVE ADSORPTION OF POTASSIUM FROM SOLUTIONS OF POTASSIUM CHLORIDE BY A NORFOLK SANDY LOAM AND BY A MARSHALL SILT LOAM

regularly with the concentration up to a certain point and then remains practically constant, the surface of the soil particles having apparently taken up the greater part of the potassium possible at this point.

The point at which the adsorption of potassium becomes constant is much lower in the case of the sandy loam than of the silt loam. The percentage of potassium adsorbed increases asymptotically as the concentration of potassium chloride decreases, and it may be concluded that the adsorption of potassium becomes practically complete at very low concentrations of potassium chloride. Chlorine was determined in several cases and was found to have remained practically unchanged.

#### EFFECT OF SIZE OF SOIL PARTICLES

Thirty-five gram portions of a Cecil clay, a Marshall silt loam, a Norfolk sandy loam, a Decatur clay loam, and a Carrington loam were placed in 200 cc. bottles with solutions of potassium chloride of about the same concentrations, and treated as in the previous experiment. The results are given in Table III.

TABLE III—EFFECT OF AMOUNT OF SURFACE EXPOSED

TYPE OF SOIL The soils in this table are arranged in order of the relative amount of surface exposed	KCl equivalent to the K per 100 cc. of solution		
	Before contact Grams	After contact Grams	DIFFERENCE Gram
Cecil clay.....	6.7350	6.4100	0.3250
Decatur clay loam.....	6.5550	6.3150	0.2400
Marshall silt loam.....	6.6950	6.2450	0.4500
Carrington loam.....	6.4300	6.2050	0.2250
Norfolk sandy loam.....	6.2580	6.1100	0.1480

As was expected, since the removal of adsorption of potassium is undoubtedly a surface phenomenon, in general the smaller the soil particles the greater was the adsorption of potassium. The classification of the different types of soil is based entirely on their mechanical analysis.<sup>1</sup>

#### EFFECT OF NATURE OF SURFACE

A clay, as is observed in the previous experiment, in spite of the fact that the size of the particles is smaller than of other types of soil does not show a correspondingly greater adsorptive power, the surface of the clay particles being undoubtedly of a different nature. Enstatite, a silicate of calcium and magnesium, when brought in contact with a solution of potassium chloride might be expected to adsorb potassium at a greater rate than chlorine, so that the resulting solution would be acid with calcium and magnesium present, as in the case of a soil. As a matter of fact, the resulting solution is alkaline to phenolphthalein and no bases other than potassium are found in the resulting solution. The nature of the surface is apparently such that chlorine is adsorbed at a greater rate than potassium.

This suggests the possibility that the selective adsorptive power of a soil may be an additive property, since a soil is composed of various minerals, so-called colloidal hydroxides of iron, alumina, organic matter, etc. The fact that the anion concentration generally remains unchanged when a soil is shaken with a solution of a neutral salt, indicates that if the selective adsorption by a soil is an additive property, the adsorptive power of the various constituents of the soil is generally greater for the cation than for the anion.

#### EFFECT OF PRESENCE OF OTHER SUBSTANCES

Portions of 35 g. each of Marshall silt loam

<sup>1</sup> Fletcher, C. C., and Bryan, H., "Modification of the Method of Mechanical Soil Analysis," U. S. Dept. Agr., Bur. Soils, Bull. 84, 1912

were placed in 200 cc. bottles with solutions containing varying amounts of potassium chloride. To some were added 10 g. of sodium nitrate, to others 10 g. of monobasic calcium phosphate. These were treated as in the previous experiment. A solution containing 28.25 g. of potassium chloride per liter in contact with calcium phosphate alone lost an amount of potassium during contact equivalent to 0.0500 g. of potassium chloride per 100 cc.

The results of analyses of the supernatant liquids are given in Table IV.

TABLE IV—EFFECT OF THE PRESENCE OF OTHER SUBSTANCES ON ADSORPTION

EXPERIMENT No	KCl equivalent to the K per 100 cc. of solution		Loss	
	Before contact Grams	After contact Grams	Per 100 cc. of solution Gram	Per cent
A—With 10 g. $\text{NaNO}_3$				
I	11.1850	10.3750	0.8100	7.25
II	8.9950	8.2650	0.7300	8.12
III	6.2400	5.6600	0.5800	9.30
IV	4.4270	3.9470	0.4800	10.83
V	2.0450	1.7140	0.3305	16.15
VI	0.8270	0.5950	0.2320	28.05
B—With 10 g. $\text{CaH}_2(\text{PO}_4)_2$				
I	11.1100	10.5700	0.5400	4.86
II	9.1300	8.6200	0.5100	5.59
III	6.3400	5.8500	0.4900	7.73
IV	4.5830	4.1200	0.4630	10.10
V	1.9930	1.5480	0.4405	22.10
VI	0.9190	0.5500	0.3690	40.15
C—With 5 g. $\text{NaNO}_3$				
I	6.3950	5.8200	0.5750	9.00
D—With 5 g. $\text{CaH}_2(\text{PO}_4)_2$				
I	6.3850	5.9000	0.4850	7.60

Table IV and Fig. II show that the presence of sodium nitrate decreases the adsorption of potassium from a potassium chloride solution by a soil up to a concen-

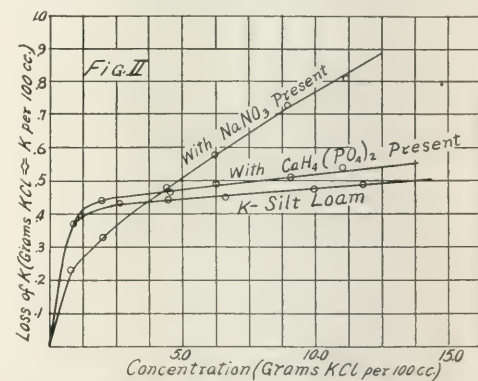


FIG. II—CURVES SHOWING THE EFFECT OF THE PRESENCE OF SODIUM NITRATE AND CALCIUM PHOSPHATE ON THE SELECTIVE ADSORPTION OF POTASSIUM FROM SOLUTIONS OF POTASSIUM CHLORIDE

tration of about 37.50 g. of potassium chloride per liter, and increases it above this concentration.

They also show that the presence of monobasic calcium phosphate does not alter the adsorption of potassium appreciably; what change there is in the form of the curve is due probably to the removal of potassium by the calcium phosphate not in solution, either by a chemical or physical reaction (adsorption).

#### CONCLUSIONS

Soils not only have the power of adsorbing dissolved salts from solution, but also of adsorbing one ion at a



greater rate than the other, or of selectively adsorbing to an extent easily determined quantitatively.

The nature of the surface of the constituents of a soil is such that the cation is adsorbed at a much greater rate than the anion.

The presence of bases of the soil (Ca, Mg, etc.) in solution, after contact of certain salt solutions with a soil, is not due to a direct chemical reaction of the salt in solution with the silicates of the soil, but to a secondary reaction of free acid, resulting from the selective adsorption of the cation, with the mineral constituents of the soil.

In general, the smaller the soil particles, the greater the selective adsorption of the cation.

The selective adsorption of the cation from a solution of an electrolyte by a soil increases with the concentration up to a certain point, and then remains practically constant, the surface of the soil particles having taken up all that it is able at this point. At very low concentrations the adsorption of the cation is practically complete.

The presence of other substances may or may not affect the selective adsorption by a soil.

BUREAU OF SOILS  
WASHINGTON

#### THE ESTIMATION OF THE LIME REQUIREMENT OF SOILS BY MEANS OF THE HYDROXIDE OF THE ALKALIN EARTHS<sup>1</sup>

By C. R. MOULTON AND P. F. TROWBRIDGE

The methods which are in use for estimating the acidity of soils are not proving to be entirely satisfactory and this gives rise to new methods and proposals for new methods. The old provisional method of the Association of Official Agricultural Chemists—shaking out the acids and acid salts with normal potassium nitrate—is open to criticism both on the score of the length of time needed for the determination and because the process does not bear any direct relation to the practice of liming soils. The method in use now, that of Veitch,<sup>2</sup> is not open to the last objection but is to the first—according to some critics—as it frequently takes a large number of determinations to fix the lime-absorbing power of the soil.

In order to cut down the length of time involved in the Veitch method, Bizzell and Lyon<sup>3</sup> have proposed a modification of R. Albert's method. The essential points of the new method are boiling the soil with an excess of  $N/10$  barium hydroxide solution and measuring the excess by means of ammonia set free from added ammonium chloride. The ammonia is distilled off and caught in  $N/10$  acid. The barium hydroxide is standardized by direct titration against the acid and a correction is made for the power of the soil to set free ammonia from ammonium chloride. Fifty cc. of barium hydroxide are used and 25 g. of soil. A fixed amount is consequently always present which may greatly exceed the amount needed by the soil or may not exceed it materially.

Now in the Veitch method it is tacitly admitted that an excess of lime water will cause more calcium oxide to be absorbed by the soil, and so the least amount that will show an excess is used as the lime requirement. Some of the effects of this mass reaction have been studied in the laboratories here in the past when an attempt was made to modify the Veitch method by titrating back the excess of lime water. The lime requirement was determined by the Veitch method. Then to fresh samples of soil various amounts of lime water were added, as 5, 10, 15, 20, 25 and 30 cc. Thus in some cases there was an excess of lime water amounting to 10 cc. and in other cases the same deficiency. It was found that when evaporating the solution with phenolphthalein a considerable deficiency required but a very few cc. more lime water to give a color than did a slight deficiency. Likewise, a great excess required but little more acid to neutralize than did a small excess. In some cases but 2 or 4 drops of acid or lime water represented a difference of 10 cc. of lime water.

An attempt was made to determine what ingredients of the soil were using this excess of lime water. It was found that thoroughly washed and ignited sea sand when used in place of soil with the Veitch method used up considerable lime water as shown by the few drops of tenth-normal acid needed to destroy the color when 5, 10, or even 15 cc. of lime water were used. Sand treated once with lime water would use up considerable amounts of lime water added subsequently after decanting and washing free of the previous addition.

Enough of this unpublished work has been quoted to show that in this laboratory it was considered to be demonstrated that an excess of calcium hydroxide increased the lime requirements of soils. It was the results of this work that led us to investigate the work of Bizzell and Lyon to determine if barium hydroxide acted any differently than did calcium hydroxide.

Lime requirements were determined on a sample of soil by the method of Bizzell and Lyon, using 50 and 100 cc. of barium hydroxide. No blanks were run on the soil as they would not effect the results found. Table I shows the results of this soil.

The Veitch method gave a lime requirement of 10,420 pounds of lime per acre foot. The Bizzell and Lyon method accurately followed gave only 85 per cent

TABLE I

G. soil No. 7b	Cc. Ba(OH) <sub>2</sub>	Cc. Ba(OH) <sub>2</sub> used by soil	G. CaO	Parts per million	Pounds per acre foot
25	50	30.40	0.06958	2783	8,350
25	50	32.90	0.07530	3012	9,036
25	50	27.29	0.06246	2498	7,495
25	100	60.00	0.13734	5494	16,481
25	100	59.14	0.13537	5415	16,244
25	100	61.20	0.14008	5604	16,811
25	35	9.80	0.02243	896	2,688
25	35	6.34	0.01451	580	1,741

of this amount, varying from 7,500 to 9,000 lbs. When double the amount of barium hydroxide called for by the Bizzell and Lyon method was used the lime requirement was increased to over 16,000 lbs., thus doubling the lime requirement.

Since about 30 cc. of hydroxide were sufficient to satisfy the soil when the determination was made as directed by the Bizzell and Lyon method, duplicate samples were run, using 35 cc. of hydroxide. In this

<sup>1</sup> Read before the University of Missouri Section of the American Chemical Society, March 6, 1914.

<sup>2</sup> *J. Amer. Chem. Soc.*, **24**, 1120

<sup>3</sup> *THIS JOURNAL*, **5**, 1011

case the lime requirement fell to about one-fourth of the first value.

The method was further tested with a different soil and by different chemists, using various amounts of barium hydroxide water, the treatment otherwise being the same as in the Bizzell and Lyon method. Table II shows the results on this second soil. A blank was run on this soil in order to be able to make a better comparison with the Veitch method. Enough ammonia was freed by the soil to represent 1.05 cc. of  $\text{Ba}(\text{OH})_2$  solution and this correction was made on the following determinations:

TABLE II					
G. soil No. 3b	Cc. $\text{Ba}(\text{OH})_2$	Cc. $\text{Ba}(\text{OH})_2$ used by soil	G. $\text{CaO}$	Parts per million	Pounds per acre foot
CHEMIST A					
25	00	1.17			
25	00	0.92	1.05 blank		
25	5	3.16	0.00858	343	1,030
25	5	3.49	0.00947	379	1,136
25	25	11.18	0.03035	1214	3,642
25	25	8.86	0.02405	962	2,866
25	50	14.11	0.03811	1523	4,597
25	50	10.41	0.02831	1130	3,391
CHEMIST B					
25	50	13.41	0.03641	1456	4,369
25	50	12.59	0.03418	1367	4,102
25	75	15.15	0.04113	1645	4,936
25	75	15.50	0.04208	1683	5,050
25	100	9.23	0.02506	1002	3,007
25	100	16.66	0.04523	1809	5,428
25	100	21.05	0.05715	2286	6,858
25	100	22.15	0.06014	2406	7,217

The Veitch method gave 6,855 lbs. of lime per acre foot, whereas the method of Bizzell and Lyon gave various amounts according to the amount of barium hydroxide used. In some cases the lime requirement found was not at all proportional to the barium hydroxide used but in general it increased as the hydroxide increased and frequently in strict proportion to the hydroxide.

In the third table the following variation of the method was used. The first two duplicates were treated as per the regular Bizzell and Lyon method until the digestion was complete when the soils were decanted upon a filter and washed three times by decantation with hot water. These washings were distilled with ammonium chloride as usual with the result that from 38 to 39 cc. of the 50 cc. of hydroxide added had not been washed out of the soil. The soil residue was again treated with 50 cc. of lime water as above and this time a further 35 to 36 cc. of the second 50 cc. of hydroxide remained with the soil. The soil residue holding about 75 cc. of barium hydroxide was then distilled and all but 13.90 cc. recovered by distillation, thus making the lime requirement comparable to that found when 75 cc. had been used in Table II.

TABLE III					
Soil 3b	Cc. $\text{Ba}(\text{OH})_2$	Cc. $\text{Ba}(\text{OH})_2$ used by soil	G. $\text{CaO}$	Parts per million	Pounds per acre foot
1st washing...	50	39.30			
1st washing...	50	38.21			
2nd washing...	50	35.59			
2nd washing...	50	36.04			
Soil.....	residue	15.34	0.04168	1666	4,998
Soil.....	residue	13.90	0.03774	1510	4,529

In Table II and all following work the barium hydroxide solutions used were standardized not by direct titration but by distillation exactly as in the determination but omitting the soil. It seems to the authors that this is the only logical method of standardization,

for then conditions are all alike in all cases. Any effect that boiling in the flasks has upon the barium hydroxide will have an influence upon both the standardization and the determination.

An extremely acid soil was selected for further study. In this case as the barium hydroxide was increased, the water added before distillation was decreased by the same volume so that the same amount of distillate would represent the same part of the whole. Otherwise the determination was carried out as usual.

TABLE IV					
G. soil 14-4-16	Cc. $\text{Ba}(\text{OH})_2$	Cc. $\text{Ba}(\text{OH})_2$ by soil	G. $\text{CaO}$	Parts per million	Pounds per acre foot
25	10	-2.20			
25	10	-2.09			
25	25	0.60	0.00120	48	144
25	25	4.46	0.00892	357	1,071
25	50	11.43	0.02286	914	2,742
25	50	10.86	0.02172	869	2,607
25	100	30.14	0.06028	2411	7,233
25	100	Lost			

Table IV gives the results on this soil. The Veitch method gave a lime requirement of 17,250 lbs. per acre foot. When 10 cc. of hydroxide were used more ammonia was recovered in the distillate than corresponded to the hydroxide. Had a blank been run on this soil it might account for the difference. The sample of soil was exhausted, and so no blank could be run. The lime requirement increases much more rapidly than does the barium hydroxide used, but not even with 100 cc. does the lime requirement reach more than a third of that found by the Veitch method.

Exactly similar results were obtained from another strongly acid soil. The Veitch method gave 18,630 lbs. of lime needed per acre foot and the Bizzell and Lyon method gave 681 and 1,032 lbs. per acre foot. A soil which was alkaline by the Veitch method at no cc. of lime water was next studied. The blank by the Bizzell and Lyon method was 56.05 cc. of acid used by the ammonia freed by the soil. Table V gives the results of this work. In all cases the soil showed a lime requirement, that is, in no case was sufficient ammonia recovered in the distillate to represent the power of

TABLE V					
G. soil 14-1-109	Cc. $\text{Ba}(\text{OH})_2$	Cc. $\text{Ba}(\text{OH})_2$ used by soil	G. $\text{CaO}$	Parts per million	Pounds per acre foot
25	10	10.72 (a)	0.029105	1,164	3,492
25	10	15.32 (a)	0.041590	1,624	4,992
25	25	15.86	0.04306	1,722	5,166
25	25	12.21	0.03315	1,326	3,978
25	50	10.82	0.03652	1,261	3,783
25	50	18.23	0.04949	1,980	5,940
25	50 (b)	7.56	0.02052	821	2,463
25	50 (b)	10.43	0.02832	1,133	3,399
25	100	28.55	0.07751	3,100	9,300
25	100	30.78	0.08356	3,342	10,026

(a) The cc. of  $\text{Ba}(\text{OH})_2$  used by the soil is expressed in terms of a tenth-normal acid which is weaker than the  $\text{Ba}(\text{OH})_2$  solution.

(b) These two determinations were run by a chemist other than the one making the others.

both the  $\text{Ba}(\text{OH})_2$  and the soil to free ammonia from ammonium chloride. Consequently when the soil blank was accounted for there remained some of the  $\text{Ba}(\text{OH})_2$  which was held back by the soil. So even with an alkaline soil some of the added hydroxide solution will be held back on distillation and will not free ammonia from ammonium chloride. The so-called lime requirement we find by this method is considerably greater for this alkaline soil than it was for the other strongly acid soils.

The behavior of some of the determinations above

was such as to raise the question whether the lime requirement could not be varied by the length of distillation of the ammonia. Some of the samples at the end of 20 minutes had used up all the hydrochloric acid in the receiving flask, showing an alkaline reaction. Five cc. more of acid were added and again the solution in the flask turned alkaline at the end of 25 minutes, necessitating a second addition of acid which was largely used up. To further test this continued freeing of ammonia, some determinations were made and the distillate was caught in different receiving flasks by means of an adapter having a two-way stopcock between condenser and receiving flask. About 450 cc. of water were used and an 800 cc. Kjeldahl. Table VI gives results on both the acid and alkaline soil.

TABLE VI

Soil	Time	Cc. Ba(OH) <sub>2</sub>	G.	Parts per	Pounds per
14-4-16	Minutes.	used by soil	CaO	million	acre foot
25 g. and 50 cc. Ba(OH) <sub>2</sub>	20	24.32	0.04864	1,946	5,838
	40	13.29	0.02658	1,063	3,189
	60	7.38	0.01476	590	1,770
	75	3.97	0.00794	318	954
	90	0.79	0.00158	63	189
	20	35.86	0.07172	2,870	8,610
14-1-109 25 g. soil and 50 cc. Ba(OH) <sub>2</sub>	40	21.31	0.04262	1,705	5,115
	60	13.24	0.02648	1,060	3,180
	75	6.99	0.01398	560	1,680
	90	3.12	0.00624	250	750
	20	39.90	0.10833	4,333	12,999
	35	24.30	0.06597	2,639	7,919
25 g. soil and 50 cc. Ba(OH) <sub>2</sub>	50	13.80	0.037466	1,499	4,497
	65	7.41	0.02012	805	2,415
	80	4.63	0.01257	503	1,509
	20	33.89	0.092005	3,680	11,040
	35	16.38	0.04447	1,779	5,337
	50	7.46	0.020254	810	2,430
25 g. soil and 50 cc. Ba(OH) <sub>2</sub>	65	0.42	0.001140	46	138
	80	0.27	0.000733	29	87

The figures shown are for the total time given. As more ammonia was freed the barium hydroxide held by the soil was decreased until at the end of 80 or 90 minutes it had been decreased to an insignificant amount which in the acid soil might have been reduced to nothing if a blank had been run on this soil. The total volume of distillate was about 450 cc. and was distributed among the aliquots about in proportion to the time of each separate collection.

A brief survey of the data presented seems to establish the fact that the lime requirement found by the method of Bizzell and Lyon is proportionate to the barium hydroxide used and not to the acidity of the soil. The lime requirement is considerably lower than when the Veitch method is used. The lime requirement varies with the length of time of the distillation and volume of distillate until a zero lime requirement is obtained.

No consideration of the speed of a method is worth while when its performance is such as is indicated by this study. However, the experience in this laboratory shows that at least as much attention on the part of the operator is needed for the method of Bizzell and Lyon as for the Veitch method. The time consumed in evaporating, and so forth, does not enter into consideration when a chemist has other work in progress.

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## A STUDY OF THE DOLOMITIC LIMESTONES OF THE ALLENTOWN QUADRANGLE

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The Allentown Quadrangle is located in the extreme

eastern part of Pennsylvania and is included between the parallels of 40° 30' and 40° 45' and the meridians 75° 15' and 75° 30' west, covering an area of about 226 square miles. It lies in Lehigh and Northampton counties with its southeastern corner in Bucks county. Most of the rocks in this section are more or less crystalline, being either sediments which have changed to slates, quartzites, schists and gneisses by varying degrees of metamorphism, or igneous rocks, such as granite and diabase which have solidified from a molten magma.

The basal complex<sup>1</sup> of the region consists chiefly of gneisses and schists. Following the formation of these deep-seated rocks occurred, a long period of erosion, after which a portion of the land was submerged beneath the sea, and sand, gravel, mud and calcareous ooze were laid down in the form of marine sediments. In these deposits, now hardened to sandstone, conglomerate, shale and limestone, are to be seen fragments of waste from the igneous and metamorphic rocks of the adjacent land. Those strata are not continuous sheets, for portions of the sea bottom were, at times, uplifted into land and the sediments that had been deposited were subjected to erosion, while other portions were still submerged. The sea in which these sediments were laid down was a body of water occupying the interior of the American continent and its eastern shore oscillated back and forth across what is known as the Appalachian province, in the eastern part of which the Allentown Quadrangle is situated. Submergence began at least as early as the Cambrian, probably as early as the Algonkian, and continued to the close of Carboniferous Time.

Several great cycles of sedimentation are recorded in the rocks of this region. The first sedimentary rocks—conglomerates, sandstones and shales—were laid down early in Cambrian time along the eastern border of the interior sea as it encroached on the sinking land. As the land was worn down and erosion became less active, the sediments became finer until in late Cambrian time very little mechanical detritus reached the sea and the deposits were mainly carbonates of lime and magnesia. This condition continued into Ordovician time with no marked break in sedimentation. During Silurian time, however, great beds of quartz sand and pebbles were laid down over the limestones of the preceding age. The Carboniferous began with the formation of marine deposits, in large part limestone, which, in the southern part of the province, are of great thickness.

The sedimentary rocks of the Quadrangle are those laid down in pre-Cambrian, Cambrian and Ordovician time.

The pre-Cambrian formations of the Quadrangle are known as the Shimer graphite schist and the Franklin limestone and are of no importance in this investigation.

The Cambrian formations are known as the Hardyston quartzite, the Leithsville limestone and the Allentown limestone.

Of the Ordovician formations, the only one of importance to us is the Coplay limestone.

<sup>1</sup> G. W. Stose, Mercersburg-Chambersburg Folio, *Geological Atlas of the United States*, No. 170.



## CAMBRIAN FORMATIONS

Conformably overlying the Hardyston quartzite there is a layer of limestone some two thousand feet thick, known as the Leithsville formation. There is abundant evidence that this limestone was laid down in shallow water; the finding of ripple marks and sun cracks in shaly layers, the occurrence of shaly layers having a wavy structure which probably indicates the surface of beds eroded by wave action and the presence of sandy layers interbedded with the limestone, all lead to the presumption that the water could not have had any great depth. Fossils seem to have been entirely absent from this formation and rather suggest a chemical origin for the limestones.

**ALLENTOWN LIMESTONE**—The upper half of the Cambrian limestone is more dolomitic than the Leithsville formation and consists of a dense bluish rock, which is very hard and brittle and does not effervesce with cold, dilute hydrochloric acid, but usually gives a strong kaolin odor when breathed upon. The only fossil thus far recognized in this formation is *Cryptozoon Proliferum*, which occurs in rounded heads varying in diameter from 1 inch to 1.5 feet. One of the principal characteristics of the Allentown is the layers of oolite which are commonly found in this formation closely associated with the fossils. As in the case of the Leithsville, it is known, by the conglomeratic basal strata and other evidences, that this limestone was laid down in rather shallow water. Mr. G. W. Stose<sup>2</sup> suggests that these formations were deposited in water so shallow that the waves oscillated the growing particles on the sea bottom and so produced the concretions.<sup>3</sup> However, the Leithsville formation, which shows ample evidence of having been deposited in shallow water, differing only from that in which the Allentown was deposited by being more muddy, is entirely lacking in oolites.

## ORDOVICIAN FORMATION

**THE COPLAY LIMESTONE**—This formation, having a thickness of 2000 ft., is the lowest of the Ordovician formations found in the Allentown Quadrangle. It consists of dark blue dolomitic limestone which, in the hand specimens, closely resembles the Allentown limestone. In the field it is distinguished by the absence of *Cryptozoon Proliferum* and by a laminated appearance on the weathered surface of many of the beds, due to their impurities. Fossil remains of cephalopods and gastropods are of somewhat common occurrence, but are not very well preserved.<sup>4</sup> Layers high in lime content sometimes show crystal faces of calcite scattered through the ground mass and will effervesce with cold, dilute acid. Near the base of the formation are sometimes found silicious, banded beds.

## STRUCTURES IN THE QUADRANGLE

The greater part of the quadrangle is covered by thick beds of sediments conformable with each other

and resting unconformably upon the pre-Cambrian gneiss which forms the basal complex of this whole region. These beds of sediment consist of successive layers of Hardyston quartzite, Leithsville limestone, Allentown limestone and Coplay limestone, all conformable with each other. Across the quadrangle, separating the Allentown limestone from the Coplay limestone, there exists a local fault line which probably originated when the gneiss, which forms the Camel's Hump, was thrust through the sediments.

The oldest rocks in the area are the pre-Cambrian gneisses forming the ridge known as South Mountain and presumably underlying the whole area. These rocks were probably formed by a sediment which grew to a thickness undetermined and in a period not definitely known. The beds were subsequently uplifted and then depressed, the depression became filled with water and during the long period following, the sedimentary rocks—the Hardyston quartzite, Leithsville limestone, Allentown limestone and Coplay limestone—were laid down. During this period of lime deposition the erosion of the surrounding land was probably very small, or at least little land derived material was transported to this region, and, since wave marks and various other indications of shallow water occur in the area, the sea which existed here could not have been of any great depth. However, the occurrence of thin shaly strata (see samples 7 and 12, Quarry "E"), and scattered seams of sandstone interbedded with the limestone shows an influx of land sediments at recurrent intervals, interrupting the formation of the limestone.

During the limestone-forming periods, instead of transporting mechanical detritus, the streams carried calcium and magnesium and other soluble salts dissolved from the decomposing rocks by the combined action of rain water and carbon dioxide. Some of the calcareous material was, no doubt, secreted from the sea water by molluscs, corals and other types of marine organisms. In the larger part of the deposits, however, few or no fossils can be found, due probably to the fact that conditions were not favorable to life in the lime-depositing sea, so there is ground for the belief that most of the limy sediment was a result of direct precipitation from water and was not produced by secretion of organisms. This almost complete absence of fossils seems to have been apparently due to the large amount of magnesium salts present in the water, although dolomitic rocks found in other parts of the region covered by the Paleozoic sea contain large numbers of fossils.<sup>1</sup>

The deposition of rock ended near the close of the Carboniferous period, the interior of the great sea was raised into land, the muds and sands were compacted and to a large extent hardened by their own weight, but the compression and folding consolidated them into firm rocks and materially altered their constitution and texture. Since that time the Allentown Quadrangle, with the exception of the southeast corner, has not been below the sea and the rocks have been subjected to erosion during the long lapse of time since then.

<sup>1</sup> B. L. Miller, Report No. 4, Topographic and Geologic Survey of Pa.

<sup>2</sup> Mercersburg-Chambersburg Folio, Geol. Atlas of the U. S.

<sup>3</sup> Mon. U. S. Geol. Surv. Vol. 11, 61 (1885), 189.

<sup>4</sup> B. L. Miller, Rept. No. 4, Topographic and Geologic Survey of Pa.

<sup>5</sup> G. W. Stose, U. S. Geological Atlas, No. 170.

## EXPERIMENTAL PART

The chemical work in connection with this investigation consists of the analyses of some one hundred samples of magnesian limestones taken from quarries so located that the whole area is well represented. All the samples were analyzed for magnesium oxide from which the equivalent magnesium carbonate was calculated, while a few samples were analyzed for silica, iron and alumina and lime. From a consideration of the results of these analyses and from deductions drawn from observations in the field we believe that the Allentown and Coplay limestones of this region were laid down as chemical precipitates and were not formed by the alteration of calcium carbonate, although we concede that probably the high percentages of magnesia were caused in part by the leaching away of calcium carbonate. We shall also attempt to explain the presence of silica in these formations and also the occurrence of quartz crystals at points where no extensive metamorphosis has taken place.

## QUARRY "A"

Quarry "A" is situated in Northampton county,  $\frac{3}{8}$  of a mile west of Georgetown Four Corners on the Centreville road and is  $1\frac{3}{8}$  miles from the northern boundary of the Quadrangle. As can be seen from Plate I, the strata here are nearly vertical and vary



PLATE I QUARRY "A"

in thickness from 2 to 8 ft. Near the center some folding and faulting occur so that it is difficult to follow the strata to the top of the quarry.

Sample	MgO	MgCO <sub>3</sub>	SiO <sub>2</sub>	R <sub>2</sub> O	CaO	Thickness of bed
A-1 a	15.41	32.20				South face
A-1-b	17.14	35.84	5.82	1.23	28.19	South face
A-1-c	16.81	35.12				South face
A-2	18.95	39.60				2 1/4 ft.
A-3	17.09	35.72				3 ft.
A-4	16.78	35.05	10.35	5.25	47.08	7 3/4 ft.
A-5	18.00	37.64				3 ft.
A-6	18.45	38.54				8 ft.
A-7	18.48	38.74				6 ft.
A-8	17.32	35.20				4 ft.
A-9	17.56	36.65	7.35	3.85	29.56	2 1/4 ft.
A-10	17.72	37.04				6 1/2 ft.
A-11	18.33	38.34				5 1/2 ft.
A-12	17.12	35.80				2 ft.
A-13	18.68	39.00				8 ft.
A-14	17.59	36.67				11 ft.
A-15	15.29	31.93				1 1/2 ft.
A-16	18.40	38.47	8.92	2.90	27.48	North face
Highest is A-13-18.68%; Greatest difference 3.39%.						
Lowest is A-15-15.29%; Average 17.51%.						

These results show quite small variation, considering the number of strata, the greatest difference being 3.39 per cent; yet the difference is large enough in our opinion to preclude the idea of replacement. The average of the CaO seems to be about 28.41 per

cent. Sample A-4 shows a very large increase in CaO with a drop of 0.8 per cent MgO from the average of the quarry. This large increase of CaO in Sample A-4 over the beds A-1-b and A-9 on both sides of it is significant and will be noted later.

## QUARRY "B"

Quarry "B" is located in Northampton county,  $\frac{1}{2}$  mile north of Broadheads on the Nazareth turnpike,  $4\frac{3}{8}$  miles from the northern boundary and  $4\frac{1}{2}$  miles from the eastern boundary of the Quadrangle. This quarry faces the west, is 700 feet long and about 30 feet high, with bedding and cleavage planes nearly



PLATE II QUARRY "B"

indistinguishable, as may be seen in Plate II. Samples were taken every 35 feet at various heights from the base.

Sample	MgO	MgCO <sub>3</sub>	SiO <sub>2</sub>	R <sub>2</sub> O	CaO	Height from base
B-1	19.13	39.98	2.36	1.97	28.89	3 ft.
B-2	20.49	42.83				10 ft.
B-3	18.68	39.04				20 ft.
B-4	19.94	41.68	7.70	3.85	28.29	15 ft.
B-5	20.16	42.14				13 ft.
B-6	19.43	40.61				3 ft.
B-7	19.98	41.76				25 ft.
B-8	20.25	42.32				5 ft.
B-9	29.35	42.53				10 ft.
B-10	20.54	42.93				8 ft.
B-11	20.47	42.78	1.74	1.17	29.43	15 ft.
B-12	19.75	41.28				10 ft.
B-13	19.88	41.55				25 ft.
B-14	19.29	40.32				7 ft.
B-15	20.37	42.57	2.45	0.93	29.50	7 ft.
B-16	20.34	42.51				7 ft.
B-17	19.85	41.49				7 ft.
B-18	18.79	39.27				7 ft.
B-19	20.16	42.14				7 ft.
B-20	19.00	39.71				7 ft.
Highest B-10-20.54%						
Lowest B-3-18.68%						

The greatest difference is 1.86 per cent MgO and the average is 19.84 per cent MgO.

The results here, as might be expected from the structure, show less variation than in Quarry "A," while the average is 2.3 per cent higher. The greatest difference is only 1.86 per cent MgO, this quarry being the most regular in the distribution of the magnesia of any that we have analyzed. The lime content is also quite regular, the greatest variation of any of the constituents being in the percentages of silica.

## QUARRY "C"

Quarry "C" is located in Lehigh County, about one hundred yards north of the Coplay station of the Lehigh Valley railroad:  $3\frac{1}{8}$  miles from the western boundary of the Quadrangle and  $6\frac{1}{4}$  miles from the northern boundary. As can be seen from Plate III, the beds here are of varying thickness, are vertical, or nearly so, and some of them are intricately folded.

This latter is quite characteristic of the Copley limestone.

Sample	MgO	MgCO <sub>3</sub>	SiO <sub>2</sub>	R <sub>2</sub> O <sub>3</sub>	CaO	Thickness of beds
C-0	13.99	37.72	.....	.....	.....	4 1/2 ft.
C-1	17.54	36.66	.....	.....	.....	2 1/2 ft.
C-2	15.10	31.56	.....	.....	.....	8 ft.
C-3	00.92	2.93	.....	.....	42.64	15 ft.
C-4	00.76	1.40	.....	.....	54.58	2 1/2 ft.
C-5	16.72	34.95	.....	.....	32.77	1 1/2 ft.
C-6	8.46	17.68	15.57	5.36	.....	2 ft.
C-7	15.57	32.54	.....	.....	53.47	3 1/2 ft.
C-8	15.46	32.31	.....	.....	32.34	1 1/2 ft.
C-9	00.87	1.82	.....	.....	.....	1 1/2 ft.
C-10	13.76	28.76	12.38	6.30	.....	1 1/2 ft.
C-11	No sample	.....	.....	.....	.....	1 1/2 ft.
C-12	16.98	35.49	.....	.....	.....	1 1/2 ft.
C-13	16.47	34.42	.....	.....	.....	1 1/2 ft.
C-14	No sample	.....	.....	.....	.....	1 1/2 ft.
C-15	15.66	32.73	.....	.....	.....	1 1/2 ft.
C-16	17.33	36.22	6.22	3.96	29.22	1 1/2 ft.
C-17	16.19	33.84	.....	.....	.....	1 1/2 ft.
C-18	14.41	30.12	.....	.....	.....	2 ft.
C-19	1.52	3.18	.....	.....	52.48	4 ft.
C-20	12.58	26.29	.....	.....	.....	4 1/2 ft.
C-21	16.77	35.05	6.44	4.60	28.64	1 1/2 ft.
C-22	14.29	29.87	.....	.....	.....	1 1/2 ft.
C-23	16.64	34.78	6.01	5.13	29.73	1 1/2 ft.

The highest is C-1—17.54 per cent MgO and the lowest is C-20—12.58 per cent MgO. This is with samples 3, 4, 6, 9, and 19 excluded. The average is about 15.58 per cent of MgO.

The very low per cent of MgO in Samples 3, 4, 6, 9 and 19 can be accounted for by an inspection of the



PLATE III—QUARRY "C"

hand samples, each of which shows crystals of calcite scattered throughout the ground mass. All these samples effervesce greatly with cold dilute hydrochloric acid and the analysis shows them to be nearly pure limestone. In connection with the high lime, the high silica and low magnesia in Samples 6 and 10 are to be noted.

#### QUARRY "D"

Quarry "D" is located in Lehigh County about 1/2 mile north of Friedensville, 4 3/4 miles from the southern

Sample	MgO	MgCO <sub>3</sub>	SiO <sub>2</sub>	R <sub>2</sub> O <sub>3</sub>	CaO	Thickness of beds
D-1	18.11	37.88	.....	.....	.....	4 1/2 ft.
D-2	19.60	40.98	.....	.....	.....	6 1/2 ft.
D-3	19.20	40.15	6.40	1.39	18.23	5 1/2 ft.
D-4	19.79	41.38	3.89	1.40	28.33	2 1/2 ft.
D-5	18.33	38.34	8.91	2.31	27.44	4 1/2 ft.
D-6	19.56	40.90	6.75	2.75	28.10	1 ft.
D-7	19.00	39.73	.....	.....	.....	3 1/2 ft.
D-8	16.80	35.13	.....	.....	.....	3 1/2 ft.
D-9	16.62	34.75	.....	.....	.....	3 1/2 ft.
D-10	16.54	34.39	.....	.....	.....	3 ft.
D-11	12.95	27.08	13.60	3.31	22.75	6 ft.
D-12	15.59	32.60	13.61	3.48	24.33	3 1/2 ft.
D-13	17.97	37.58	.....	.....	.....	4 1/2 ft.
D-14	17.69	36.90	.....	.....	.....	3 1/2 ft.
D-15	18.62	38.93	.....	.....	.....	7 1/2 ft.
D-16	16.39	34.27	.....	.....	.....	1 1/2 ft.
D-17	19.09	39.92	.....	.....	.....	4 ft.

Highest D-4—19.79% MgO  
Lowest D-11—12.95% MgO

Greatest difference 6.84% MgO  
Average 17.87% MgO

boundary and 5 1/2 miles from the western boundary of the Quadrangle. This location is an abandoned zinc

mine and in Plate IV it can be seen that the beds are nearly vertical while the hand specimens show considerable weathering.

This quarry shows the greatest difference in magnesia of any of the quarries, yet the average is within about 0.3 per cent of that of Quarry "A," located near the northern boundary of the Quadrangle. These beds are characterized by rather low lime content and high silica. In particular, Samples 11 and 12 show, for reduced magnesia, an increase in silica rather than in lime, as might be expected.

#### QUARRY "E"

Quarry "E" is located in Northampton County, 1/4

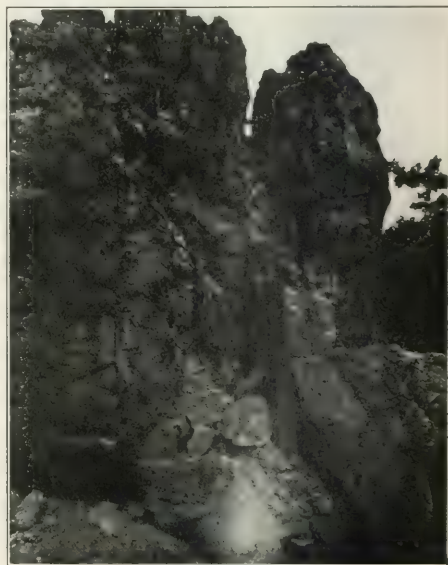


PLATE IV—QUARRY "D"

mile west of Quarry "B," being a cut of the Lehigh and New England railroad. As may be seen in Plate V, the beds are sharply inclined to the north.

Sample	MgO	MgCO <sub>3</sub>	SiO <sub>2</sub>	R <sub>2</sub> O <sub>3</sub>	CaO	Thickness of beds
E-1	16.97	35.47	.....	.....	29.03	29.03
E-2	18.00	31.35	8.71	4.53	28.26	2 1/2 ft.
E-3	11.45	23.93	12.25	1.30	16.62	2 1/2 ft.
E-4	14.59	30.49	.....	.....	.....	1 1/2 ft.
E-5	13.60	28.42	.....	.....	.....	1 1/2 ft.
E-6	13.87	28.99	8.08	5.39	24.54	4 1/2 ft.
E-7	7.58	15.85	.....	.....	.....	1 1/2 ft.
E-8	12.65	26.44	.....	.....	.....	4 1/2 ft.
E-9	15.77	32.96	.....	.....	.....	1 1/2 ft.
E-10	14.71	30.74	.....	.....	.....	1 1/2 ft.
E-11-a	16.38	34.23	.....	.....	.....	6 1/2 ft.
E-11-b	13.18	27.55	21.52	8.10	18.08	6 1/2 ft.
E-12	6.70	14.00	.....	.....	.....	1 ft.
E-13	14.64	30.60	.....	.....	.....	1 1/2 ft.
E-14	14.51	30.33	.....	.....	.....	1 1/2 ft.
E-15	18.36	38.37	5.20	3.08	31.42	2 1/2 ft.
E-16	16.01	33.45	2.55	3.76	33.63	2 1/2 ft.
E-17	9.75	20.38	.....	.....	.....	2 1/2 ft.
E-18	16.86	35.24	.....	.....	.....	6 1/2 ft.
E-19	14.84	31.02	.....	.....	.....	9 ft.
E-20	14.76	30.85	.....	.....	.....	.....

Highest E-15—18.36% MgO

Lowest E-8—12.65% MgO, excluding Samples 3, 7, 12, 13

Greatest difference 5.71% MgO

Average 15.10% MgO

Samples 3, 7, 12 and 13 are excessively low in magnesia. Inspection of the hand specimens shows that



3 and 17 contain crystals of calcite throughout the ground mass, while 7 and 12 are clay shales and give off an earthy odor when breathed upon.

The difference in content of lime is also to be noted, ranging from 16.62 per cent in E-3 to 33.63 per cent in E-16, a difference of 17 per cent. There is also considerable variation in the silica.

#### CONSIDERATION OF RESULTS

The comparatively small variation in the averages of the contents of magnesia in these several quarries, located so close together and the sharp differences in the amounts of magnesia and lime occurring in the various strata in the same quarry, lead us to the belief that the rocks of this section were laid down by chemical precipitation rather than by alteration of the limestone; a fact which tends to support this theory is the thinness of the strata in the various quarries. This, together with the occurrence of clayey layers as in "Quarry E" and the fact that we find ripple marks and other evidences of shallow water commonly occurring in this formation shows that the Paleozoic sea was very shallow and probably receded frequently.

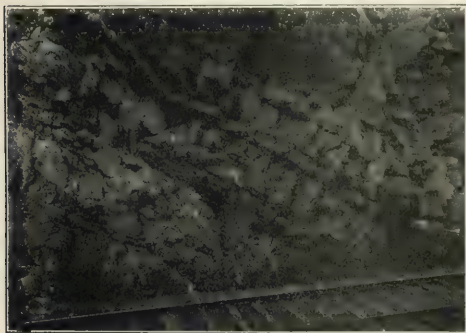


PLATE V—QUARRY "E"

Hence this area could not have been far removed from land, from whence it would receive, by drainage, waters containing not only carbonate of lime in solution, but also carbonate of magnesia. Provided the two carbonates were in solution at the same time, the shallowness of the sea would facilitate their precipitation because the evaporation taking place at the surface would throw the salts out of solution while at the same time this same shallowness would prevent them from going back into solution as they settled to the bottom.

The theory that the rocks in this section were originally of marine origin, that is, that they were more or less pure calcium carbonate, which was afterward removed from solution and was replaced by carbonate of magnesia, would, in the first place, presuppose a sea of enormous extent and great depth: a sea large enough in extent so that the waters flowing from the surrounding igneous rocks could not carry any appreciable amount of magnesia to this area. During this time, then, limestone would be deposited, not in thin strata, but in thick ones, which, as can be seen from an inspection of the region, do not occur.

In order to replace the carbonate of lime with carbonate of magnesia, there would be required a body of water containing a comparatively large content of soluble magnesium salts. In consideration of the fact that in water free from carbonic acid, magnesium carbonate is about sixty times as soluble as calcium carbonate and that in water saturated with carbon dioxide the magnesium salt is about twenty-seven times as soluble as the corresponding calcium salt, we can not comprehend how percolating waters, or the lower layers of sea water, can enrich the rock with magnesia by extracting the lime. And even if this were possible, due to some selective action of the solution which in turn might depend upon its content of other soluble salts, we do not believe that a compact rock would result. This conclusion has also been reached by E. Blackwelder.<sup>1</sup>

In case such replacement could take place it is reasonable to assume that such replacement would be quite uniform within narrow limits; but in our investigation we find just the opposite the case. For instance, in Quarry "C," Sample 2 carries 15.10 per cent; Sample 3, 00.98 per cent; Sample 4, 00.67 per cent; and Sample 5, 16.72 per cent of magnesia. In each of these cases the content of calcium carbonate fluctuates accordingly, being very high where the magnesia is low. Other instances can be seen in Quarries "A" and "E." From such evidence we do not believe that the high magnesia is a result of secondary action but that it was originally laid down in this condition.

It may be and probably is true that some of the limestone in this region has been enriched in magnesia by the solution of portions of the lime by percolating waters saturated with carbon dioxide; still why these waters should shun the strata represented by Samples E-3 and E-4, leaving a high content of magnesia, we can not understand, when the strata on both sides are lower in calcium carbonate and higher in magnesium carbonate. If any enrichment has taken place, it must have been locally and did not affect the region as a whole.

The scarcity of fossils in these rocks is also significant. Both the Allentown and the Copley limestones are rather deficient in organic forms of life and those that are found are not very well preserved. In a way this proves our contention that the rocks are chemical precipitates, for it shows that the original material of the rocks has not been withdrawn from the sea water by organic forms of life. While it may be possible that the life which existed has been obliterated, yet it is a well known fact to biologists that increasing percentages of magnesium salts cause stupefaction of such organic forms as sea anemones and the like and it may well be that waters of high magnesia content are not conducive to the growth of lime-secreting forms of life.<sup>2</sup>

Another evidence of chemical precipitation is the

<sup>1</sup> "Origin of the Big Horn Dolomite of Wyoming." *Bull. Geol. Soc. of Am.*, Dec., 1913.

<sup>2</sup> Tullberg, *Arch. Zool. Exper. et Gen.*, 10 (1892), 11; Redenbaugh, *Amer. Naturalist*, 29 (1895), 399; Journ. Royal Micro. Soc., 1895, p. 385; Gerould, *Bull. Mus. Comp. Zoology*, Harvard, 29 (1896), 123.

occurrence of oolitic layers interbedded with the Allenton limestone and closely associated with the only fossil recognized in this formation, namely the *Cryptozoon Proliferum*. It is conceded by various authorities that these formations are caused by chemical precipitation<sup>1</sup> and in addition they are evidences of the shallowness of the sea during their formation. A shallow sea seems to be necessary to the formation of limestone, for the ocean depths are covered with red clay.

Lastly, even at the present time we have waters which contain comparatively large quantities of magnesia as compared with the lime. For instance, Thresh<sup>2</sup> gives analyses of waters which are derived from argillaceous beds of the early Eocene period and which underlie clays in which the content of carbonate of lime ranges from 1.75 to 39.00 parts per 100,000, while the magnesium carbonate ranges from 0.35 to 11.75 parts per 100,000. These figures are in ratios which compare favorably with the ratios found in the rocks under investigation.

In concluding, then, that these formations were caused by the precipitation of carbonates of magnesia and lime at the same time, we must consider the presence of the silica. If our hypothesis is correct that no replacement of calcium carbonate by magnesium carbonate subsequent to formation has taken place; also that no enrichment of the magnesia by the leaching away of the lime has taken place—at least to no appreciable extent and only locally—it must be that the silica content of the rock was deposited at the same time as the other constituents.

From the analyses it will be seen that the silica content varies with the amounts of magnesia and lime present. In most cases we find that low percentages of magnesia are accompanied by higher percentages of silica and these are increased, in some cases, by the low content of lime as in Sample E-11-b, where the magnesia is lower than the average, the silica is very high and the lime is much lower than the average of the lime. If these substances were in solution originally, some such ratios might readily be expected from the differences in their solubilities. An inspection of the hand specimens shows that no silica can be detected and it is probable that the silica is distributed quite evenly through the rock. This, together with the variation, tends to support the theory of precipitation. That silica has, in the past, been carried in the waters of this region is evidenced by the finding of quartz crystals north of Camel's Hump or about in the center of the Quadrangle. The formation of quartz crystals from solution has been noted in many cases.<sup>3</sup> Silica is more or less soluble in water,<sup>4</sup> the amorphous forms more readily than the crystallized forms, and the solubility is appreciably increased by the presence in the water of dissolved carbon dioxide and particularly by the presence of dissolved carbonates of the alkali

metals and those of the alkaline earths. Dieren<sup>1</sup> asserts that there is a definite relationship between the alkalinity of water and the dissolved silica which can be expressed by the formula  $x - y = Ky$ .

The formation of quartz crystals from a water solution presupposes the united action of heat and pressure, both of which can be readily assumed to have been present. The pressure was due to the weight of the overlying material, of which it is safe to say there has been removed by solution 15,000 to 20,000 ft. from this region. The heat was due partially to pressure, but more particularly, we believe, to friction caused by the upheaval and bending of the strata. In several places, notably at Coplay, this bending of the strata has been so great that contractions of as much as from 5 ft. to 1 ft. have taken place. In such cases enormous amounts of heat must have been generated, enough in several instances to have caused the rock to have become partially plastic, since in the folds at Coplay no fissuring has taken place even in the case of strata, which have been almost bent back upon themselves. The heat which would cause the smooth bending of the rock would, in our opinion, be much more than necessary to produce quartz crystals from a water solution, since, according to Maschke,<sup>2</sup> the amount of heat necessary is equivalent to something over 180° C., and according to K. Chrustschoff<sup>3</sup> 240° to 300° C., and according to Ramsay and Hunter<sup>4</sup> about 200° C.

As a matter of interest we have calculated the amount of heat that would be generated by a column of magnesian limestone, 15,000 ft. in height and 1 sq. ft. in cross section, slipping a distance of one foot in a minute. We have taken the coefficient of friction to be 0.65 and the specific heat of magnesian limestone to be 0.217. The amount of heat liberated, then, is enough to raise the temperature of 217 pounds of rock 1° C., which, added to the rise in temperature due to pressure alone, would give heat enough to satisfy the requirements for crystallization. Also since the specific heat of limestone is high, it is safe to assume that most of the heat would be confined close to the region at the point of slippage. The limestone in the neighborhood of the Camel's Hump and generally throughout the region shows more or less metamorphism but at no point is this enough to indicate the formation of quartz from a state of fusion.

From the facts and assumption above outlined we believe it is safe to conclude that the silica found in the region was originally in a solution and was deposited when the other materials were laid down and was not deposited as a result of subsequent seepage of waters.

In conclusion, we believe that the following facts support the theory of chemical precipitation:

I—The magnesia content does not vary greatly over the region.

<sup>1</sup> F. W. Clarke, "Data of Geochemistry," pp. 116, 528.

<sup>2</sup> "Examination of Water and Water Supplies."

<sup>3</sup> Spezia, G., *Jour. Chem. Soc.*, **76** (1899), Pt. 2, 300; Clarke, F. W., "Data of Geochemistry," p. 344; Levallois, F., *Ceramique*, **16**, 135.

<sup>4</sup> Rogers, W. B. and R. E., *Amer. J. Sci.*, [2] **5**, 1848; Headon, W. P., *Ibid.*, [4] **16**, 1903; Hilgarde, E. W., *Ibid.*, [4] **2**, 1896; Comey, A. M., "Dictionary of Chemical Solubilities," Clarke, F. W., "Data of Geochemistry," pp. 457-8.

<sup>1</sup> *Compt. rend.*, **155**, 707.

<sup>2</sup> *Proc. Ann.*, **145**, 549, 146, 90.

<sup>3</sup> *Amer. Chemist*, **3**, 1873, 281, *Compt. rend.*, **104** (1887), 602, *Neues Jahrb.*, **1897**, Pt. 1, 240.

<sup>4</sup> *Rept. British Assoc. Adv. Sci.*, **1882**, p. 239.

II—The strata are separated at several points by beds of nearly pure limestone.

III—Few fossils are found in the rocks of the region.

IV—The occurrence of oolitic layers in the Allentown limestone.

V—The silica seems to have been in solution and

was laid down when the rest of the constituents were precipitated.

VI—We find waters containing carbonates of magnesia and lime in about the same proportion that we find them in the rocks of this region.

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## LABORATORY AND PLANT

### DETERMINATION OF CARBON IN STEEL BY THE DIRECT COMBUSTION METHOD

By WM. BRADY

Received July 27, 1914

This method consists of the direct combustion of the metal in oxygen. The carbon dioxide obtained is absorbed in a known excess volume of barium hydroxide solution, the precipitated barium carbonate and the excess barium hydroxide are rinsed into a flask, and the latter is titrated with standard hydrochloric acid using phenolphthalein as an indicator. This titration subtracted from a blank titration of the standard acid against the same volume of barium hydroxide used, gives a measure of the carbon converted to carbonate.

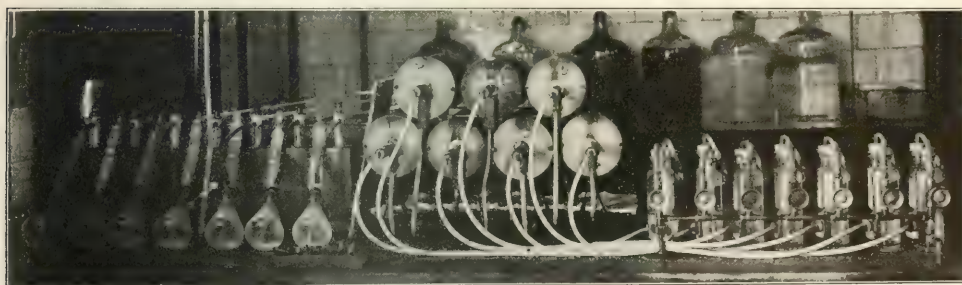
#### APPARATUS

**PURIFYING TRAIN**—The only purifying train required before the furnace is a wash bottle containing a solution of KOH of about 1.27 sp. gr., and an 8-inch tower containing soda lime. The KOH solution, besides absorbing any  $\text{CO}_2$  which might be present in the

in the forward part of the combustion tube. In order to keep the forward stopper cool, however, a small cylindrical platinum basket filled with asbestos is connected to the rubber stopper at the entrance of the tube, by means of a copper wire. Removal of the stopper to insert a boat removes this basket at the same time. The other end of the combustion tube is kept cool by being filled from the catalyzer to the extreme end with broken pieces of quartz tubing. This packing furthermore reduces the necessary time of aspiration.

**COMBUSTION APPARATUS**—Both gas and electrically heated furnaces are used. In either case the temperature is maintained at about  $960^\circ$  to  $1000^\circ$  C. There are occasions when more heat is required, for example, with very low-carbon steel when the drillings are not as fine as they should be. In such cases temperatures up to  $1100^\circ$  C. may be used. A  $3/4$ -inch quartz tube 24 inches long is used.

**BOATS**—Nickel or platinum boats are used. Care must be exercised when using platinum to carefully protect the boat with the alundum. Nickel boats



FRONT VIEW OF BATTERY OF COMBUSTION FURNACES

oxygen, also furnishes means of judging the rate of flow of this gas. No precautions are necessary to prevent access of water vapor, but a bubble tube containing granulated zinc of about 20 mesh is inserted between the furnace and the absorption apparatus to absorb any  $\text{SO}_3$  formed from the oxidation of sulfur in the steel.

**MATERIAL FOR LINING BOATS**—Alundum, "R R Alundum, 60 mesh, alkali-free, specially prepared for carbon determination" is used.

**CATALYZERS**—Platinized asbestos mixed with broken pieces of quartz tubing is used as a catalyzer in the hot part of the combustion tube just following the position occupied by the boat. No catalyzer is used

must be thoroughly burned in a stream of oxygen until they give no blank before being used.

**ABSORPTION TUBE**—A combination of an Erlenmeyer flask of 500 cc. capacity, taking a No. 6 stopper, a row of nine small bulbs with a stem bent at an angle parallel to the side of the Erlenmeyer flask, a small glass entrance tube and a No. 6 two-hole rubber stopper is used to absorb the  $\text{CO}_2$  formed by the combustion. A heavy wall rubber tube connects the exit end of the zinc bubble tube with the small glass entrance tube which is inserted through one of the holes in the No. 6 stopper. The stem of the row of small bulbs, or bulb tube, is inserted through the other hole of the stopper. The charge of 80 cc. of  $\text{Ba}(\text{OH})_2$  solution is placed in



the flask, and the No. 6 stopper, holding the two tubes, is inserted in the neck of the flask. By inclining the flask on its side so that the bent stem reaches the bottom edge of the same, the Erlenmeyer acts as the large bulb of a Meyer tube, and the gases entering through the small entrance tube force the barium hydroxide up into the nine small bulbs. At the end of the determination the flask is set on its bottom so that the bulb tube is in a vertical position, the stopper is loosened and a stream of water is forced into the upper, or exit end, of the bulb tube. This rinses the precipitated  $\text{BaCO}_3$  and the excess  $\text{Ba(OH)}_2$  into the flask. The stem of the bulb tube is then rinsed off, and the flask withdrawn. Another flask containing a fresh charge of  $\text{Ba(OH)}_2$  is attached in its place, the boat containing the burnt steel is replaced with another containing a new sample, and the next determination is thus started with no loss of time for adjustment of the oxygen. An experienced operator can thus keep a number of furnaces under continuous operation without touching the oxygen valves.

#### REAGENTS

**OXYGEN**—Linde oxygen, in cylinders containing 100 cu. ft. of gas at approximately 1800 lbs. pressure, is used. A reducing valve reduces the pressure to about 15 lbs., and supplies all the furnaces shown in the photograph.

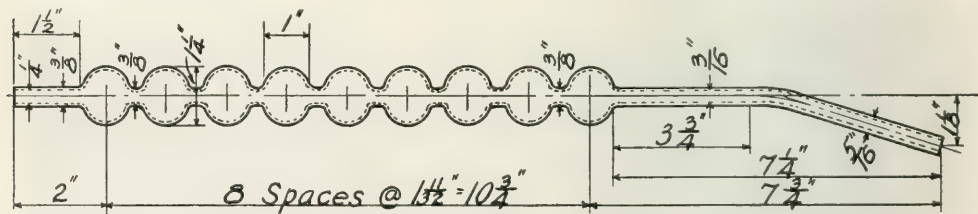
**STANDARD HYDROCHLORIC ACID**—8.125 cc. of HCl of 1.20 sp. gr. diluted to 1000 cc. standardized by means of a standard steel of known carbon content.

**BARIUM HYDROXIDE SOLUTION**—15 grams of  $\text{Ba(OH)}_2$  crystals per 1000 cc. distilled water. The precipitate

continuous determination of carbon in regular heats, billets and extra or special samples. With medium- or high-carbon steel the sample is sieved, and that which passes a 10-mesh and remains on a 40-mesh sieve is taken for combustion. With low-carbon steel it is preferable to use a 20-mesh sieve in place of the 10-mesh. By alterations in the method of placing the sample in the boat, rate of supply of oxygen, and temperature of the furnace, an experienced operator can burn drillings much larger than those above specified.

#### METHOD

Place 2 grams of fine drillings in a V-shaped depression made in a refractory lining of a suitable combustion boat. By means of an overflow pipette, place exactly 80 cc. of  $\text{Ba(OH)}_2$  solution in a 500 cc. Erlenmeyer flask. Connect this flask to the special absorption tube at the exit end of the combustion train. Then insert the boat containing the sample in the combustion tube, which is maintained at  $960^\circ$  to  $1000^\circ$  C., by means of a suitable furnace. Replace the stopper at the entrance end of the combustion tube, and, by means of a needle valve, turn on the current of oxygen. Regulate the supply of oxygen so that there is a continuous bubbling in the wash bottle with such rapidity that the individual bubbles can just be counted for a short time. Continue the flow at this rate for 25 minutes. No adjustments are necessary. At the end of this time loosen the stopper in the Erlenmeyer flask, and, without withdrawing the stem of the absorption tube, rinse out the latter thoroughly. Finally rinse off the stem of the absorption tube, and with-



BARIUM HYDROXIDE TUBE FOR CARBON COMBUSTIONS

of  $\text{BaCO}_3$  is allowed to settle and the clear solution decanted. In use the solution is kept in a large bottle on an overhead shelf and siphoned over as required into an 80 cc. overflow pipette. Both the bottle and pipette are protected from  $\text{CO}_2$  by a soda lime tube.

**PHENOLPHTHALEIN**—2 g. dissolved in 1 liter of ethyl alcohol.

#### FACTORS INFLUENCING DIRECT COMBUSTIONS

The size of the drillings, the rate of flow of the oxygen and the temperature of the furnace are the three important factors in direct combustions. The rapid method, wherein samples are burned at such high temperatures that fusion takes place, is sometimes used where speed is required. The method used in routine work, however, is a slower method but one which experience has shown to be best suited to the continuous operation of a battery of combustion furnaces. The method here given is used for the

draw the flask. Add several drops of phenolphthalein, and titrate with standard HCl to the disappearance of the pink color.

A blank determination is carried out exactly as described above, using the same volume of  $\text{Ba(OH)}_2$  solution, but with no steel in the furnace. The difference between the amount of standard acid equivalent to the  $\text{Ba(OH)}_2$  used, as determined by this blank titration, and the amount used in the actual titration, multiplied by the carbon value of the acid, corresponds to per cent carbon.

#### NOTES

A standard should be run every time the acid reservoir supplying the burette is refilled, or at least daily in each furnace. Blanks should be run each time the bottle of distilled water or barium hydroxide is refilled.

Under continuous operating conditions,  $\text{SO}_2$  formed by oxidation of sulfur in the steel, combines with water

vapor to form sulfuric acid which condenses in the packing in the exit end of the combustion tube. The zinc tube prevents any sulfuric acid thus formed from entering the absorption tube, but the bulk of it condenses in the cold end of the combustion tube. It is important to burn out this accumulation after making about 50 combustions, in the following manner: Disconnect the stopper from the exit end of the tube and pull the latter forward so that the exit end is heated to the temperature of the furnace. Keep a slow stream of oxygen passing through the tube until the fumes of sulfuric anhydride are no longer visible. This takes but a few minutes each day, and ensures better results.

When the supply of oxygen is correctly adjusted about nine minutes should elapse between the time the boat is inserted and the first appearance of turbidity in the absorption flask.

The titration with standard hydrochloric acid should be accompanied by thorough agitation of the flask. The last 5 or 10 cc. should be run in rather slowly.

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### AN APPARATUS FOR THE ANALYSIS OF COMPLEX GAS MIXTURES<sup>1</sup>

By GUY B. TAYLOR

Received July 7, 1914

In making a study of the gases evolved from coal at various temperatures, it has been found necessary to make analyses of gases of very complex composition. The usual forms of apparatus described in the gas manuals are accurate enough for mixtures containing only a few simple constituents, or for technical work where great accuracy is not required. Most of these methods require separate portions for the estimation of hydrogen and saturated paraffin hydrocarbons, since one complete combustion permits of the calculation to hydrogen and one hydrocarbon only. Even commercial coal gas contains appreciable quantities of homologs higher than  $\text{CH}_4$ , and calculation of the combustion data to hydrogen and methane only is open to question.

Bone and Wheeler<sup>2</sup> have described an apparatus for the analysis of complex gases in which the absorptions are carried out in a single pipette with fresh reagent for each absorption and in which the changes caused by these absorptions are measured at constant volume by difference in pressure. In the apparatus described here, use of the Bone and Wheeler method of absorption has been combined with the usual form of compensated burette (A), Fig. 1, a copper-oxide U-tube for the estimation of hydrogen and carbon monoxide (C), and a slow-combustion pipette (B) for burning hydrocarbons. The absorption vessels (D, E) dip into a wooden trough containing mercury. The reagents are introduced by means of curved pipettes under the lower edge and after use are discharged into G by applying suction at g.

Although the surface exposed to the gas is not very great, this is largely offset by the use of fresh reagents

so that the absorption proceeds rapidly. Of the slower-absorbing reagents, cuprous chloride for CO has been eliminated and alkaline pyrogallate for absorbing oxygen in the concentration usually found in gases, to which this apparatus is particularly adapted, does not consume much time. The small quantity of reagent has the advantage of reducing to a minimum solution of other gases not intended to be absorbed by that reagent. For example, fuming sulfuric acid appreciably attacks paraffin hydrocarbons higher in the series than  $\text{CH}_4$  and may cause errors in either the Hempel or Orsat apparatus.<sup>1</sup> Using about 3 cc. fuming acid in the apparatus here described, 73.5 cc. of Pittsburgh natural gas ( $n = 1.16$  in  $\text{C}_n\text{H}_{2n+2}$ ) passed into the pipette 5 times and allowed to stand 5 minutes gave a contraction of 0.05 cc.; similarly 40 cc. of an oil gas ( $n = 1.61$ ), in which homologs higher than methane predominated, showed 0.07 cc. contraction, neither of which much exceeds the error of reading.

### DETERMINATION OF HYDROGEN AND CARBON MONOXIDE BY FRACTIONAL COMBUSTION WITH COPPER OXIDE

It has been found in this laboratory that for crude, unwashed gases from low-temperature distillations of coal, the methods for estimating hydrogen depend-

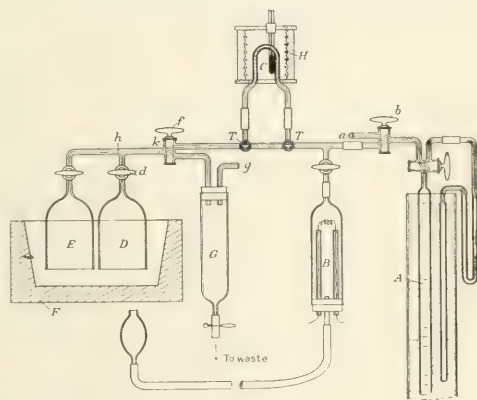


FIG. 1

ing on the catalytic action of palladium, such as palladium black or colloidal liquid absorbents, are unsatisfactory and in most cases fail entirely.

If a mixture of CO,  $\text{H}_2$ , and hydrocarbons of the series  $\text{C}_n\text{H}_{2n+2}$ , in absence of oxygen, be passed over copper oxide heated to about  $250^\circ \text{C}$ ., the CO may be burned quantitatively to  $\text{CO}_2$  and the hydrogen to water, while the hydrocarbons are untouched, in which case the contraction in volume is equal to the hydrogen present, and the  $\text{CO}_2$  formed equals the CO in the mixture. Nesmijelow<sup>2</sup> determines these two gases simultaneously with CuO in the presence of oxygen, in which case the equivalent oxygen necessary for the oxidation disappears, the CuO acting in intermediary or

<sup>1</sup> Published by permission of the Director, U. S. Bureau of Mines.

<sup>2</sup> Jour. Soc. Chem. Ind., 27 (1908), 10.

<sup>1</sup> Compare Burrell and Seibert, Bulletin 42, Bureau of Mines, p. 46.

<sup>2</sup> Zeit. anal. Chem., 48 (1909), 232.

catalytic capacity. Since the oxide itself furnishes the required oxygen this is unnecessary.

In Fig. 1, the inverted U-tube C is about 5 mm. internal diameter and contains 3-4 g. of a mixture of fine and coarse cupric oxide, which is prevented by glass wool plugs from getting into the capillary connections. One capillary is sealed on before the tube is filled and the other afterward. The gas volume of the tube need not exceed 2 cc. It is seldom necessary to renew the copper oxide if the tube is removed and gently heated over a free flame, while a current of air is being blown through it, until the bright specks of reduced copper become oxidized. It is advisable to revive the oxide thus after three or four times use. The inverted position is chosen to prevent danger of cracking from water running back into the heated part.

**TEMPERATURE OF THE CuO**—Jaeger,<sup>1</sup> the originator of the method for hydrogen, set the temperature at 250° C.; Ubbelohde and de Castro<sup>2</sup> fix it at 270°, which is the temperature advocated by Dennis.<sup>3</sup> The method of taking temperature by putting a thermometer bulb in an oven and leaving a long emergent stem may be many degrees in error. The exact temperature that can be used will depend upon the nature of the hydrocarbons present. With CH<sub>4</sub> only, 300° is probably not too high, but at this temperature there is danger of oxidation of the higher homologs of CH<sub>4</sub>. We have obtained satisfactory results with the thermometer bulb next the U-tube in a small electrically heated oven at 275° for gases in which the average value of  $n$  in C<sub>n</sub>H<sub>2n+2</sub> was as high as 1.65.

This oven may be simply constructed in any laboratory and a few preliminary experiments will determine what temperature on the thermometer between 250° and 300° works best for the gases to be analyzed, then by noting the current required the heating conditions may be exactly reproduced for each analysis. For constructing the heater take two glass tubes, 35 mm. diameter, and bind them together side by side. Around the two tubes wrap several thicknesses of heavy paper. Over the paper wind No. 20 nichrome or "Climax" wire 2 mm. between turns for about a 10 cm. length on the tubes. This gives an oval-shaped heating coil around which the oven is to be built. After fastening the ends, which should be twisted double to serve as leads, wrap a layer of wetted, thick asbestos paper tightly around the coil and fasten it with copper wire wound between the resistance wire turns. Then cover with a thin paste of magnesium-oxide-sodium-silicate cement and paste on several layers more of asbestos paper. The oven may be dried out at once over a free flame, which bakes the wire covering hard and chars the inside paper so that the glass tubes may be removed. The oven is completed by wrapping loosely several layers of asbestos board for heat insulation, covering the ends and cutting a slit in one of them for the entrance of the U-tube.

**TESTS OF THE METHOD**—In Table I are given some of the results obtained by the method of fractional combustion, which shows that not only may hydrogen and carbon monoxide be burned in the presence of methane without danger of oxidation of the latter but also in the presence of high concentrations of higher paraffins. The hydrogen was prepared by electrolysis and passed over a glowing platinum spiral to remove traces of oxygen. The CO was prepared from oxalic and sulfuric acids, purified and analyzed by combustion with oxygen. Hydrocarbon gas (a) was Pittsburgh natural gas in which the average value of  $n$  in C<sub>n</sub>H<sub>2n+2</sub> determined from the combustion data was 1.16. Analyses of this gas in the Bureau's laboratories by fractional condensation have shown that it contains both ethane and propane.<sup>1</sup> Gas (b) is a natural oil gas ( $n = 1.61$ ) in which homologs higher than methane predominate,

TABLE I

CO	Cc. taken		Cc. found	
	H <sub>2</sub>	C <sub>n</sub> H <sub>2n+2</sub>	CO <sub>2</sub> formed = CO	Contraction = H <sub>2</sub>
12.30	0.0	35.0 a	12.35	0.0
34.10	0.0	34.6 a	33.70	0.0
17.35	0.0	49.3 b	17.30	0.0
0.0	20.45	38.8 b	0.0	20.45
0.0	15.20	59.2 b	0.0	15.25
0.0	50.40	39.1 b	0.0	50.30
4.40	7.10	44.0 b	4.40	7.10
14.80	23.75	43.5 b	14.55	23.80

In an artificial mixture containing approximately 52 per cent H<sub>2</sub>, 15 per cent CO, and 17 per cent Pittsburgh natural gas, was found by analysis 14.6 per cent CO by absorption with ammoniacal cuprous chloride and 14.65 per cent CO by the CuO combustion method, 52.0 per cent H<sub>2</sub> by CuO after absorbing CO, and 52.1 per cent determined simultaneously with CO by the combustion method.

The time required for the complete burning of the hydrogen and carbon monoxide does not seem to be a function of the quantities present, as much as the nature of the gas mixture. For ordinary illuminating or producer gas, the hydrogen is usually completely removed in 6-10 slow passes over the CuO. With some low-temperature coal distillates, not scrubbed, we have consumed as high as 40 minutes removing 3-5 cc. In general, when the contraction due to the burning of the hydrogen has ceased the CO may be assumed to have been also completely oxidized, unless it be present in much greater concentration than the hydrogen, in which case passage through the CuO tube should be continued some minutes longer. An increase in volume occurring at any time during the operation may be due to combustion of higher hydrocarbons.

In general, it may be stated that the time required for the estimation of these two constituents by this method is shorter than any direct absorption method for CO alone.

#### PROCEDURE FOR ANALYSIS OF COAL GAS

The reagents needed are 30 per cent KOH, potassium pyrogallate solution, and fuming sulfuric acid. The first two are prepared in quantity and stored in protected bottles with glass siphons leading to rubber

<sup>1</sup> Jour. Gasbeleuchtung, 41 (1898), 764.

<sup>2</sup> Ibid., 54 (1911), 810.

<sup>3</sup> "Gas Analysis," L. M. Dennis (Macmillan, 1913), p. 201.

<sup>1</sup> Burrell and Seibert, Loc. cit., pp. 91-96.



tubes provided with pinch cocks and glass tips. These tips are turned up at the end (Fig. II) and the reagent delivered by gravity into the absorption pipette.

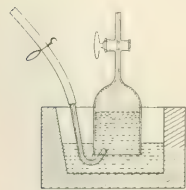


FIG. II

For washing out the pipette, bottles of water and 5 per cent sulfuric acid are similarly arranged.

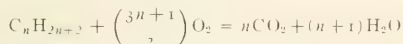
At the beginning of an analysis the tube C is filled with air and the T stopcocks turned so as to by-pass C. The burette (whose walls are, of course, kept wet), the vessels B, D, E, and all connecting capillaries are filled with mercury. The sample is taken into the burette at *a*. The calibration marks on the burette include the volume from the stopcock *b*. The volume of the capillary space from *b* to *d* is also known. After ascertaining the volume of the sample, run the gas into D and by lowering the leveling bulb on the burette, set the mercury meniscus on a mark just under the stopcock *d*. Now introduce 3–5 cc. KOH, pass the gas into the pipette several times, bring back to the mark *d*, and read the contraction in volume equal to the CO<sub>2</sub> in the gas. Bring the KOH to *k* and discharge the reagent into G, and after washing D reset the mercury thread at *d*. The reading should not have changed.

Introduce 2–3 cc. of fuming acid by means of a curved pipette and absorb the illuminants. After discharging the acid, the wash water, which is acid, should be run through the bore of the stopcock at *k* and a little way into the capillary connecting with the burette, in order to make sure that no alkali is left to foul the tubes. At this point the added precaution should be taken of thoroughly rinsing both pipettes with dilute acid. Reset to the mark *d* and introduce about 1/2 cc. KOH for absorbing the fumes from the previous reagent. Extreme care must now be taken to avoid any alkali rising above *d* until after the hydrogen has been determined. Without removing the KOH introduce 5–6 cc. pyrogallate solution and absorb the oxygen.

The gases remaining (CO, H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, etc.) are determined by combustion. Communication through C having been established by properly turning the T stopcocks, a number of passes of the gas into the pyrogallate pipette D are made to remove completely the oxygen in C. Now bring the heater over C and establish the temperature at about 275°. Pass the gas back and forth between the burette and the vessel E until there is no more contraction in volume. Bring the mercury from E to the point *h*, remove the heater from C and allow to cool. The observed contraction equals the hydrogen. Since the gas is free from oxygen, the CO<sub>2</sub> formed may be absorbed in the pyrogallate and equals the CO present in the sample. Turn the T stopcocks back to their original position. Discharge the reagent from D and thoroughly wash with dilute acid. Run the residual gas completely into D, filling all the capillaries again with mercury. Draw into the burette 95–100 cc. of oxygen and

without noting its exact volume run most of it into E, connect C again and bring back the oxygen through it into the burette to wash out the combustible gases, leaving C filled with oxygen. Open the by-pass, cutting out C, and bring the mercury to *b* for measurement of the volume of the oxygen, which is then run into the combustion pipette B. Bring the gas in D back into the burette and make the usual slow combustion for hydrocarbon,<sup>1</sup> noting the contraction and CO<sub>2</sub> produced. Attention is called to the fact that the gas must always be run into the oxygen and never in the reverse order, since the higher hydrocarbons are decomposed with deposition of carbon by the glowing platinum wire. In the method here described of clearing the copper-oxide tube of hydrocarbons, care must be taken never to obtain an explosive mixture. If the gas volume of the tube does not exceed 2 cc. and at least 95 cc. of oxygen are used, there is no danger of this occurring.

The combustion data may be calculated to CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> by applying equations based on contraction and CO<sub>2</sub> produced,<sup>2</sup> but perhaps a better way is that suggested by Earnshaw<sup>3</sup> and used in this laboratory. The general equation for the combustion of hydrocarbons of the series C<sub>n</sub>H<sub>2n+2</sub> is



If the volume of C<sub>n</sub>H<sub>2n+2</sub> be called V, the CO<sub>2</sub> produced A, and the contraction C, then

$$A = nV$$

$$C = \left( V + \frac{3n+1}{2} V \right) - nV$$

or

$$C = V \left( \frac{n+3}{2} \right)$$

$$V = \frac{2C - A}{3} \quad \text{and} \quad n = \frac{A}{V}$$

The above detailed procedure has been given in order to indicate a method of manipulation that saves time. To an operator analyzing a certain type of gas in routine work short cuts will suggest themselves. As an illustration of the possibilities of this apparatus for technical work, the following analyses of coal gas drawn from the mains of the city of Pittsburgh were made in about 1 hour each (Table II):

TABLE II ANALYSIS OF PITTSBURGH COAL GAS

	I Cc.	II Cc.	Per cent	I	II
Taken for analysis	67.15	86.65	CO <sub>2</sub> .....	2.45	2.80
Absorbed KOH.....	1.65	2.15	Illuminants.....	7.90	7.50
Absorbed fuming H <sub>2</sub> SO <sub>4</sub> .....	5.30	6.45	CH <sub>4</sub> .....	0.10	0.10
Absorbed pyrogallate	0.05	0.10	H <sub>2</sub> .....	38.80	38.80
Contraction, { CuO.....	26.00	33.60	CO.....	12.50	12.60
CO <sub>2</sub> produced {.....	8.40	10.00	C <sub>n</sub> H <sub>2n+2</sub> .....	35.20	35.00
Contraction { Combustion	48.85	63.85	N <sub>2</sub> .....	2.45	2.60
CO <sub>2</sub> .....	25.75	34.50		100.00	100.00

The average value of *n* in C<sub>n</sub>H<sub>2n+2</sub> is about 1.08. Had one complete combustion been made after re-

<sup>1</sup> See the gas analysis manuals of either Dennis or Hempel.

<sup>2</sup> Burrell and Seibert (*loc. cit.*, pp. 80–86) have called attention to the fact that a correction for molecular volumes of carbon dioxide and ethane should be applied in calculating from combustion data, but unless the concentration of hydrocarbons is great, the correction will be small.

<sup>3</sup> Jour. Frank. Inst., Sept., 1898. See also Porter and Ovitz, Bureau of Mines, Bull. 1, p. 24.



### "SMOKING"

1—Fire one door at a time and wait until fire is in good shape before charging the other door.

2—Leave furnace door slightly ajar for about 2 minutes after firing.

3—Fire frequently at regular intervals and in small quantities.

4—Keep the fires clean.

5—Carry a level surface over entire grate. Avoid thin or bare spots on grate.

6—Break lumps of coal to fist size.

The monitor can be made to operate many arrangements automatically and in coal furnaces these may be steam jets, dampers, draft-producing fans, and similar apparatus.

### THE SMOKE AND FUME PRECIPITATOR

In previous<sup>1</sup> papers I have described a method of precipitating fumes, dust and smoke from gases by means of the corona discharge. The portable instrument shown in Fig. II may be used to precipitate any kind of dust, fumes or smoke from gases and will clean about 100 cu. ft. of gas per minute. The main part of the apparatus is a small high voltage transformer, and although it can be used as a monitor or recorder it is just as well adapted for precipitation work.

There are many cases where gases should be cleaned of smoke or fumes before being analyzed, such as in many of the CO<sub>2</sub> recorders. The portable precipitator is designed for problems of this kind. In common with the monitor and recorder it consists of a transformer T, using about 150 watts or less of energy operating from any convenient alternating lamp socket. The transformers are designed to give about 26,000 volts on the high tension side of the circuit. The chamber containing the precipitating electrode is not shown. It is very small and simple, however, and can be made of a metal that will not be corroded by the given fumes or smoke. The electrodes are so small that they can easily be placed on balances and weighed. Fine smoke, such as that from cigarettes, is precipitated with the greatest of ease.

### THE SMOKE AND FUME RECORDER

Figs. II and III represent different types of smoke and fume recorders, Fig. II representing the portable type. Like the monitor (Fig. II is a combination monitor and recorder, B being a bell and F the indicating sign "FUMING" or "SMOKING"), the recorder consists of a high tension low wattage (about 100 watts or even less in many instances) transformer. On the high tension side there are at least two high resistance gaps in parallel, one being in the smoke or fumes and the other leading to a condenser (H and J being the condenser electrodes). When little smoke or fumes is present in the stack the electrical discharge takes place there. Depending on the length of the gaps, there is a certain density of the smoke or fumes that throws the discharge over to the condenser,

charges it and thus closes an electrical circuit or operates a watch or clock.

It is thus easily seen that the electrical circuit can be made to operate many furnace appliances and the watch can be used to record in various ways. The record can be a trace or an integrating time record

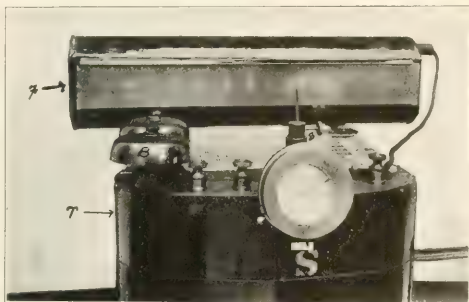


FIG. II

as is shown in Figs. II and III, these recorders giving the total time (the watch running only during fuming or smoking that exceeds a certain predetermined density) that the furnaces have fumed or smoked since the recorder has been set.

The thermostat, monitor, precipitator and recorder are based almost entirely upon an alternating current transformer, the efficiency and reliability of which is very well known. No chemical or moving parts

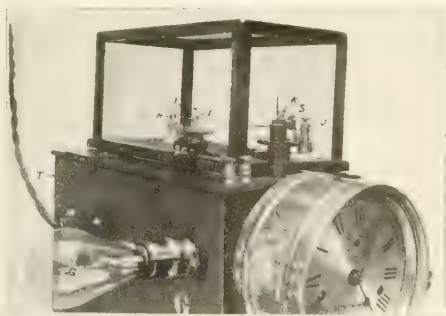


FIG. III

are used. There is no wear except in the contact points where the monitor sign and bell circuit is made and broken. No adjusting is required after the gaps are set except the tension on the upper plate of the condenser by means of a vertically moving rod S. It is thus seen that these forms of apparatus are extremely simple and they can be made entirely fool-proof by enclosing all the high tension parts in a case as in Fig. III. To make adjustments it is then necessary to remove the case and then the primary current is broken at S, C.

MECHANICSBURG, PA.

<sup>1</sup> Proc. Am. Inst. of Electrical Engineers, June 27, 1913, Journ. Frank. Inst., Sept., 1912.



## ADDRESSES

AIR OZONATION<sup>1</sup>

By MILTON W. FRANKLIN

The subject of air ozonation may be divided into three heads: I—Ozone as an adjunct to ventilation; II—Destruction of odors from industrial plants such as glue factories, fertilizer plants, slaughter houses, fish marts, etc.; III—Adjunct to refrigeration in the practice of cold storage and food preservation.

## I—VENTILATION

The application of ozone to ventilation has attracted much attention recently owing to the publication of a multitude of conflicting opinions concerning its merits. This confusion is due to several circumstances. In general, the proponents of ozone have claimed too much and have advanced many contentions, either insufficiently supported or in the very nature of things insusceptible of proof. On the other hand, the opponents of ozone have attacked these claims with great energy and often have gone so far as not only to deny any usefulness whatever to ozone, but positively to affirm its harmfulness and dangerous character. In any cases the attacks on ozone have been directed against imaginary claims that were never made and much of the evidence against ozone is based on laboratory experiments which bear little or no resemblance to actual working conditions and therefore can scarcely be considered as authentic.

A careful and unbiased investigation of all the evidence accessible in the extant literature in connection with the theory and principles of ventilation hygiene must result in the conviction that ozone, properly applied, is capable of advancing greatly the art of ventilation and that it is incapable of harming persons exposed to its influence.

At the IX Congress for Heating and Ventilating held in Cologne in June, 1913, two notable papers were read: one by Prof. Czaplewski,<sup>2</sup> and the other by L. Von Kupffer,<sup>3</sup> which presented in detail the present status of the question and which elicited the following comment from Dr. Ing. H. Rietschel, the honorary president of the Congress:

"\*\*\*\*\* We have heard with conviction that ozone has been used in numerous cases with the best of results for ventilating plants and that it can be used for such purposes; also that in the diluted state in which it is to be used it cannot be considered as being harmful. We shall, therefore, devote our undivided attention to ozone and its application for ventilating purposes."

The subject of ozone in ventilation was treated by the present writer in a paper presented at the Fourth International Congress on School Hygiene,<sup>4</sup> in which were described some experiments which demonstrated that many odors arising from organic sources were destroyed and not masked by ozone. It was shown that

1—Ozonized air does not merely mask offensive odors of varied nature, but that it actually destroys them.

2—The odors of some common food materials (onions, garlic, and limburger cheese) are destroyed by ozonized air.

3—The odors resulting from decayed raw food materials, fish, eggs, meat and oysters, are destroyed by ozonized air.

4—The offensive odors of fertilizers are destroyed by ozonized air.

5—Several definite chemical compounds which contribute to the odor of feces, perspiration of feet, rancid butter, sauer-

kraut and limburger cheese namely, skatol, valerianic acid and butyric acid, are also destroyed by ozonized air.

6—The persistent odor of tobacco smoke as absorbed by the clothing is destroyed by ozonized air and the yellow color produced by blowing smoke through cloth is bleached by ozone.

The following tabulation presents some of the materials upon which the experiments were performed:

	Odor before treatment with ferrous sulfate solution		Odor after treatment with ferrous sulfate solution	
	With air	With ozone	With air	With ozone
Onions....	Strong onion	Strong ozone	Strong onion	None
Garlic	Strong garlic	Strong ozone	Strong garlic	None
Limburger cheese...	Strong limburger	Strong ozone	Strong limburger	None
Decayed fish	Very offensive	Strong ozone	Very offensive	None
Decayed eggs....	Very offensive	Strong ozone	Very offensive	None
Decayed meat....	Very offensive	Strong ozone	Very offensive	None
Decayed oysters...	Very offensive	Strong ozone	Very offensive	None

According to the modern theory of ventilation, the only baneful factors in "vitiating" air are heat, moisture and odors. If the air is stagnant and motionless its powers to absorb heat and water are not utilized fully; hence, a fan which circulates the air generally adds much to the comfortableness of a poorly ventilated space. The ancient beliefs that excess of carbonic acid gas and deficit of oxygen accounted for the distress attendant upon inadequate air supply have been dispelled by the published labors of Haldane, Hill, Pfuegge, and others. It has been shown that in the worst cases the available oxygen is far in excess of the demand and that CO<sub>2</sub> is harmless in the concentrations likely to be met. The conviction once prevalent that organic "crowd poisons" were the guilty factors likewise has been abolished. Billings, Mitchell and Bergey<sup>5</sup> have added much to the knowledge of this aspect of ventilation. The most recently demolished belief was that bacteria existed as a menace in rebreathed air. The works of Pfuegge,<sup>2</sup> Chapin,<sup>3</sup> Doty,<sup>4</sup> and of Winslow and Robinson, have fairly disproven this contention.

The modern practice of ventilation, then, clearly is concerned only with absorbing the almost invariable quantity of heat produced per capita of room occupants, of removing the moisture transpired, and of destroying the odors generated and which are due to the presence of people, animals and organic substances, including foodstuffs, especially when in a state of putrefaction.

Heat and moisture absorption have received weighty consideration from the engineering profession and may readily be accomplished with accuracy and certainty in any given set of conditions. Odor elimination, by no means the least important, may be accomplished best through the agency of ozone. Supplying too great an amount of air in a ventilating system constitutes an engineering and hygienic error as well as does supplying too little air. Correct engineering practice consists in accomplishing an end in the least costly manner compatible with correct performance of function; and too much air means dangerous drafts, waste, and inefficiency. Ozone renders possible the elimination of odors which often cannot otherwise be removed at all, or possibly only by the providing of a prohibitive excess of air with the attendant probability of drafts and low economy. But primarily, ozone is most useful in those myriad instances where idealized ventilation systems are sim-

<sup>1</sup> Presented at the Semi-annual Meeting of the American Society of Heating and Ventilating Engineers, Cleveland, July 10, 1914

<sup>2</sup> *Indust. Eng. Chem.*, Aug. 1, 1913.

<sup>3</sup> *Ibid.*, Aug. 16, 1913, p. 605.

<sup>4</sup> *Heating and Ventilating Magazine*, N. Y., Vol. X, Nos. 10 and 11, Oct. and Nov., 1913.

<sup>5</sup> Billings, Mitchell and Bergey, "Composition of Expired Air and Its Effect upon Animal Life," Smithsonian Inst., 1895.

<sup>2</sup> Pfuegge, *Zeit. f. Hyg. u. Infekt. Krankh.*, 49, 363 (1895)

<sup>3</sup> S. Chapin, "Sources and Modes of Infection," p. 314.

<sup>4</sup> Doty, *Med. Record*, N. Y., Nov. 2, 1912, p. 891.

ply beyond the question. In these all too numerous, though unfortunately inevitable places, where perfect ventilation is impossible, ozone will produce a condition of the air unattainable by any other known means. It imparts a freshness and "tang" to the air, rendering it comparable with that in the most favored natural localities.

Ozone in general destroys and does not mask organic odors as has been shown above.

It remains then only to know that ozone is inoffensive and incapable of harming persons breathing it, in such quantities as are used in ventilation, before justifying and recommending its use.

Cramer<sup>1</sup> stated at the Frankfurt Congress for Heating and Ventilating:

"In earlier times we assigned to ozone a poisonous influence on animal organisms, while recent investigations have shown that the ozone is poisonous only when made chemically and not pure. A mixture of chemically pure ozone with atmospheric air can, if the percentage of ozone is not too concentrated, never hurt an organism, as statements from doctors and scientists show. Only in very concentrated form does it attack the lining of the mucous membrane."

No single instance of harm to a person from the proper use of ozone in ventilation has been recorded, but, on the contrary, all adverse opinions have been deduced, by inference, from laboratory experiments performed with very high concentrations, while all efforts to produce harm experimentally with weak ozone have failed. Jordan and Carlson report that twenty-six animals, exposed for fourteen days, during nine hours each day, to concentrations high enough to cause irritation of the eyes and nose, suffered no ill effect whatever. Hill cites the cases of the numerous workers in the London underground tubes, who have shown no ill effect in three years. Gminder cites the unharmed workers in the spinning mills at Reutlingen. Erlwein<sup>2</sup> says:

"It is a fact at any rate that there have never been proven cases of sicknesses of a serious character due to breathing ozone air. Special attention is called to a large water sterilization plant operating for more than ten years, where the working force is constantly moving in an atmosphere which is more strongly mixed with ozone than is ever found in actual ozone ventilation installations. There has never been a case where these persons have been forced to be on sick-leave due to the high ozone concentrations in the plants."

Numerous similar instances of prolonged proper use of ozone without a single complaint are in existence.

Efforts to disinfect occupied rooms have shown that ozone, in concentrations sufficient to produce sterility of the cultures, is irritating to the mucous membranes of the respiration tract and in fact will produce death in guinea pigs, but as pointed out above, sterilization of atmosphere has little sanitary value and it must be remembered that no known method of room disinfection can be practiced in the presence of room occupants. Sulfur dioxide, hydrocyanic acid and formaldehyde would produce death in guinea pigs more rapidly than would ozone. It has been shown that ozone in high concentrations is a local mechanical irritant, but there is no evidence to justify the opinion that it is injurious in low concentrations.

Toxicologists recognize two distinct classes of poisons: namely, physiological or chemical poisons and mechanical poisons. The former act by being absorbed into the system and causing trains of phenomena through the nervous mechanism; the latter act merely by causing local destruction of the tissues with which they come into direct contact. Strychnine is an example of a chemical poison; its action is dependent only on the quantity ingested and is wholly independent of its concentration. One

grain administered internally will cause death, whether it be taken pure or copiously diluted with water. An example of a mechanical poison is sulfuric acid; its only action is a local destruction of bodily tissues, and a quantity which would cause death, if administered concentrated, might be taken with impunity when accompanied by a sufficient diluent. Ozone has been shown to be a mechanical irritant, but to deduce the result that because strong ozone is harmful, weak ozone also must be harmful, is equivalent to arguing that because 50 per cent oxygen breathed for a certain period will cause death from inflammation and edema of the lungs, 20 per cent oxygen, such as we inspire at every breath, is also poisonous.

Experiments conducted by Jordan and Carlson to determine whether or not ozone in low concentrations, somewhat higher than might be used in ventilation, is harmful, have resulted in the following conclusions:

"All the animal groups showed some increased body weight, but the increase during the ozone period is practically the same as during the control period. Slight differences are of no significance. Hence, as regards appetite and body weight, the results of the tests are negative, the ozone appearing to have neither a favorable nor an unfavorable influence. This applies also to the general conditions of the animals. The cats did not seem disturbed, even when the ozone concentration caused some restlessness in the rabbits, guinea pigs and rats. In all other respects the animals appeared to be normal."

This is a convincing demonstration of the harmlessness of even too high ozone concentrations. The animals were exposed for fourteen days to ozone, following a period of fourteen days confinement for control observation, but in spite of the prolonged close confinement and extremely inadequate ventilation (sixteen cubic feet per hour per animal), they thrived as well during the second fourteen days with rather too strong ozone as during the first fourteen days.

So far as is definitely known, the value of ozone in ventilation is not due to any beneficial effect upon the human economy but to the circumstance that it destroys much that may be objectionable or harmful in foul air. The air is not better because it contains ozone but because this ozone signifies the absence of such organic effluvia as otherwise would be obnoxious.

The well established fact that ozone is a powerful germicide in the presence of water has led to much experimentation and speculation on its possible power of destroying the bacteria in the air. Wyszokowitz<sup>3</sup> experimented with chemically formed ozone and found a diminution in the air bacteria, but owing to the many possible errors in his method of procedure his results are frankly admitted to be of little value. He attributed the effect observed to the simultaneous formation of acid, which rendered the soil unsuitable for the growth of bacteria. Froelich<sup>2</sup> found some diminution in air bacteria with strong ozone. Sonntag<sup>3</sup> found no effect of ozone in low concentrations on dry bacteria, but with extremely high concentrations (13.5 grams per cbm.) the bacteria were destroyed. Konrich also obtained negative results with cultures dried on strips of filter paper and on glass rods. Labbé and Oudin produced diminution in the bacterial count but they admit that their results are of little importance, owing to possible sources of error.

Bail<sup>4</sup> has experimented quite extensively and states:

"Even strong ozonization of the enclosed air with circulation never allowed the beginning percentage of the air as regards bacteria to be reduced in a conclusive manner. The bacteria in the air were determined either on open agar plates or else by passing known quantities of air through gelatine. Passing air, ozonized as much as possible in the apparatus, through tubes having powdered bacteria or through loose sand containing

<sup>1</sup> Quoted from Czaplewski, *Ibid*.

<sup>2</sup> *Zeit. f. Sauer u. Stickstoffindustrie*, 1913, Nos. 7 and 8.

<sup>3</sup> Mitt. a. d. Bremer Heilanstalt, Wiesbaden, 1890.

<sup>2</sup> *Electrotech. Zeit.*, 1891, p. 340.

<sup>3</sup> *Zeit. f. Hygiene*, 8, 1890.

<sup>4</sup> *Prag. med. Wochenschr.*, 1913, No. 17, p. 216.

bacteria, gave no conclusive indication of an effective action of the ozone on the bacteria. Experiments to change the humidity of the air by evaporating water during ozonization and circulation produced no changes in the results."

Jordan and Carlson found little or no effect on plated and dried cultures with low ozone concentrations, but in four tests on the bacteria suspended in the air, three showed an average decrease of 53 per cent and one showed an increase of 10 per cent. The writer has shown a decrease in the bacteria suspended in the air but the ozone concentration probably was relatively high.

The general evidence of laboratory experimentation seems to indicate that low concentrations of ozone, at least, have no consistently demonstrable action on dried bacteria, whether in cultures or floating in air. On the other hand, there is a considerable amount of evidence to the effect that in storage cellars and similar places the growth of fungi, molds, and similar microorganisms is impeded, if not totally repressed, by even weak ozone concentrations applied for prolonged periods. A possible explanation is afforded in the work of Trillat,<sup>1</sup> who has shown:

"That the transport of pathogenic microbes in the air is effected especially by the damp which contains, in an infinitesimal state, traces of gas-aliments. Moreover, it would seem that the air, when it fulfills certain conditions of dampness, of chemical composition, of temperature, and of age of microbes, is capable of being fertilized directly by the contact of a microbial source. Up till now it was thought, according to numerous observations, that for microbes to be transported by the air it was necessary to project them into it by some mechanical action, such as pulverization or any other means, the effect of which would be to detach them from their support. Contrary to this notion, Trillat and Fouassier have established experiments demonstrating that when the superposition of certain factors takes place, the sowing of the air is performed in the same manner as that of a bouillon culture, merely by the play and movement of the invisible vesicles which constitute the humidity of the air. In an infinitely feeble volume of about one hundred-thousandth of a cubic millimeter, these tiny drops are uninfluenced by the action of the force of gravity. They are always mobile under the influence of the least variation of temperature. M. Trillat and Fouassier have shown how the contamination of the air takes place in a closed and tranquil space, without the intervention of the presence of dust or of any mechanical means, as was believed up to the present time."

It seems probable that the gradual lessening in the bacterial count in the air of places that have been ozonized for some time is due, not to direct influence of ozone on the bacteria, but to the alteration in the air as a culture medium and also to the fact that the myriad cracks and crevices in the walls, ceilings, hangings, furniture, etc., which harbor cultures that constantly supply bacteria in the air, are gradually exhausted. This would account for the discrepancy between laboratory tests of brief duration and actual prolonged trials.

#### II—ODOR DESTRUCTION

**CASEIN**—In addition to the odor destruction tests outlined above and already published, further tests have since been made with casein and with tobacco smoke. The casein tests were undertaken with the object of destroying the odors arising from a factory producing about 500,000 lbs. casein per month. This material had a very bad, nauseating odor. In drying the material, air is passed over it or through it, and this takes up part of the disagreeable odor. This air then passes up a stack and out into the atmosphere, where it proves a nuisance to the neighborhood. The problem is to destroy the odor before it passes up the stack.

Tests were made on the effluvium from the casein to determine whether ozone would affect it. For this purpose about 15

grams were put into a Petri dish under a bell jar. When the air had become saturated it was caused to displace the water in a Wolff bottle. A measured amount of this effluvium was then allowed to mix with a measured amount of ozonized air of known concentration. Several tests were made, using various quantities of ozone, any odor due to excessive ozone being removed with ferrous sulfate. In each case the odor due to casein was destroyed. The least quantity of ozone which sufficed was 1.84 mg. per liter of effluvium; 1.75 mg. per liter left a slight trace of the odor. The results are presented herewith.

1—1 l. of effluvium was entirely deodorized by 0.47 mg. of ozone, with a distinct excess of ozone.

2—11 l. of effluvium were entirely deodorized with 0.41 mg. of ozone or 0.037 mg. per l. with excess of ozone.

3—14 l. of effluvium were deodorized with 0.171 mg. of ozone or 0.012 mg. per l. with excess of ozone.

4—0.0057 mg. ozone per liter of effluvium materially lessened the odor but did not destroy it entirely.

The proportion of air to casein in the experiment was less than in the most unfavorable case that the factory conditions exhibit. The casein used was in a much more advanced state of decay and probably had odors that were far stronger than are ever obtained at the factory. Complete elimination of the odor was the object in the experiment, and this was obtained at will. The qualitative tests which preceded the quantitative tests demonstrated that actual destruction and not masking of the odor was attained.

**SMOKE**—The destruction of the odor of stale tobacco smoke and of old moist cigar stumps has always constituted a most graphic illustration of the power of ozone. Rooms in which much smoking has occurred retain the odor of tobacco in the walls, hangings and furnishings, and this odor is enduring and persistent. Experiments in which it was shown that the odor imparted to cheese-cloth by tobacco smoke could be destroyed by ozone have been published in the previously cited paper.<sup>1</sup> There seems to be some difference of opinion, however, regarding the effect of ozone on the smoke present in an occupied room during the actual smoking, and where the ozone is of such strength as to be comfortably borne by the room occupants.

Hill and Flack<sup>2</sup> noted that the apparent density of the smoke diminished and that the odor disappeared. Kisskalt, Schwartz and Münchmeyer<sup>3</sup> noted a lessening in the smoke density and total disappearance of the odor. Cramer<sup>4</sup> states with regard to experiments performed on a large scale:

"All that could be clearly demonstrated was the fact that the smoke haze became appreciably lighter and that the pungent characteristic of the smoke disappeared, rendering it no longer irritating to the eyes."

Czaplewski<sup>5</sup> states:

"In our own tests with stronger ozone concentrations, cigarette smoke was entirely destroyed in a room so as not to be perceived by a person entering the room from the outside. There was no 'after' smell and tobacco smoke on clothing is disposed of by ozone."

Smoke consists of particles of carbon and of various volatilized pungent and aromatic substances. Only the latter give taste, smell and irritating properties to smoke, the carbon contributing most of the visibility. The volatile elements in smoke exist in the gaseous form, *i. e.*, in a state of molecular subdivision, but the carbon particles exist in the shape of molecular aggregates, each of infinite size compared with the molecules themselves, otherwise they would not be visible. Ozone can combine only with the volatile elements in smoke. It thus renders it odorless, tasteless, and incapable of causing irritation,

<sup>1</sup> *Heating and Ventilating Magazine*, N. Y., Vol. X, Nos. 10 and 11.

<sup>2</sup> Hill and Flack, *Proc. Roy. Soc., Ser. B*, **84**, p. 404.

<sup>3</sup> Kisskalt, Schwartz and Münchmeyer, *Chemiker Zeit.*, **1912**, No. 129.

<sup>4</sup> *Gesundh. Ing.*, **1909**, p. 498.

<sup>5</sup> Czaplewski, *Ibid.*

<sup>1</sup> *Sixtieth Congr. Appl. Chem.*, **1917**.



but it cannot burn the carbon which in any event is totally inert and harmless. Numerous tests with actual smoke have shown this to be true.

In my own tests I have observed that when the ozone is turned on in a smoke-laden atmosphere the density of the smoke lessens and the odor and pungency disappear, the smoke being entirely undetectable excepting for its visibility. For some time I have suspected that the apparent diminution in visual density might be due to stirring up of the air by the fan which is attached to all the ozonators with which I have experimented in this direction. Some experiments were performed to determine whether or not ozone actually diminished the smoke density. Wolff bottles of 2 l. capacity, and furnished with a tubulure at the base, were filled with water. One of the necks was stoppered and the other attached by a rubber tube to a glass funnel inverted over a quantity of burning tobacco. The tobacco was burned on a thin, flat iron plate by means of a gas burner placed underneath. The funnel was supported with its rim about  $\frac{1}{2}$  inch above the plate and directly above the tobacco. When the tubulure was opened and water permitted to flow from the Wolff bottle, the air which replaced the water flowed under the edge of the inverted funnel and over the burning tobacco, whose smoke was carried along with the air. In this manner each of two bottles was half filled with a dense cloud of smoke. One of these bottles was then connected to the ozone line and the remaining water replaced by ozonized air, leaving about  $\frac{1}{2}$  inch of water in the bottom of the bottle. Into the other bottle atmospheric air was introduced in the same manner. The bottles were then shaken to cause the water to mix the smoke and air thoroughly, and the bottles were placed side by side on a shelf and observed after various periods of time. The results are presented in the following tabulation:

I Test No.	II Ozone mg.	III 15 min.	IV 30 min.	V 1 hr.	VI 4 hrs.
1.....	1.05	Slightly clearer	Slightly clearer	Marked clearing (slight)	Marked clearing
2.....	0.92	Slightly clearer	Slightly clearer	Slightly clearer	Marked clearing
3.....	1.10	No difference	Slightly clearer	Slightly clearer	Slightly clearer
4.....	1.13	clearer(?)	Slightly clearer	Marked clearing	Marked clearing
5.....	0.96	Slightly clearer	Slightly clearer	Slightly clearer	Marked clearing (slight)

The remarks under Columns III, IV, V and VI refer to the bottles containing smoke, air and ozone, directly compared with the corresponding bottles containing only air and smoke. The tobacco was of a standard inexpensive "cut plug" variety sold in ten cent packages and was rather sweet, strong and moist. The amount of tobacco was completely burned, the entire gaseous products of combustion entering the Wolff bottle. There was considerable condensation on the funnel at first, but later this decreased greatly, as ascertained on weighing the funnel, and the results given are of the later tests. The smoke in the bottles was much denser than could be obtained in any room by persons smoking.

It will be seen that in the bottle containing ozone the smoke, in general, cleared sooner than that in the bottle containing only air. The difference, though always unmistakable after several hours, was only occasionally quite marked. The amount of clearing after the lesser periods of time was so slight as often to be questionable, but in general it can be said that the ozone makes a slight reduction in the smoke density. In each case the smoke settled slowly in a cloud, leaving the top of the bottle clear. The "conglomeration" noted by Cramer<sup>1</sup> was seen only in one test (No. 3) and then only faintly.

It might be concluded from the above tests that ozone is capable of lessening somewhat the visual density of tobacco smoke, but when it is remembered that the ozone concentra-

tion was about 1 gram per cmb. it hardly seems probable on first thought that the clearing noted when ozone at a concentration not exceeding 1 mg. per cbm. is turned into a smoky room, is due alone to the action of the ozone. However, a consideration of the quantities involved indicates that this may well be true. In the tests the products of combustion of 2 grams of tobacco were collected in the space of 2 l. in approximately 2 minutes. This would be equivalent to burning 41 kg. tobacco in a room of 41 cbm. (12 ft.  $\times$  12 ft.  $\times$  10 ft.) in 2 minutes. Five men smoking pipes in such a room would burn only 4.3 g. in the same period. Thus the ratio of tobacco consumption in the above described laboratory tests and in this hypothetical case is approximately 10,000 : 1, while the ratio of the ozone concentrations is only 1,000 : 1, or in a similar actual case occurring in practice the amount of ozone would be about ten times more in proportion to the tobacco than in the tests described. Besides this there would be approximately 10,000 times as much air for the smoke to diffuse into and a marked clearing action is exercised by the air, which may be intensified by the action of the ozone. The estimates of the amounts of tobacco consumed are based on measurements of ten pipes and on timing different smokers. The average amount of tobacco (of the kind used in the experiments) held by the pipes was 1.62 g. and the average time of smoking was 38 minutes. In all cases the odor of the smoke was markedly or even completely removed, leaving it odorless, tasteless and with no power to irritate the mucous membrane of the eyes, nose, or mouth.

Fragments of cloth were cut into strips 5 cm.  $\times$  8 cm. and suspended in a bell jar having a tubulure at the bottom and a neck at the top. The latter was connected on an aspirator and tobacco smoke was drawn in at the tubulure. After the smoke from 2.5 grams of tobacco had permeated the cloth strips the latter were removed and examined; they smelled strongly of tobacco. They were then replaced in the bell jar and ozonized air was drawn through for varying periods of time. The concentration was 1.03 mg. per cbm. The results were as follows:

Test No.	Material	Result	Time
1	Cheese-cloth (thoroughly washed)	Thoroughly deodorized	9 min.
2	Cheviot (cut from an old suit)	Thoroughly deodorized	29 min.
3	Satin (cut from lining of old suit)	Thoroughly deodorized	18 min.
4	Duck (new)	Thoroughly deodorized	6 min.

No. 1 became most strongly odorous with the same exposure as the others. After a rest of 12 hours No. 2 experienced a slight, though distinct, return of odor, which, however, disappeared finally with 5 minutes' additional ozonization. The comparative thickness and microscopic complexity of the cloth undoubtedly accounts for this phenomenon.

### III—COLD STORAGE AND FOOD PRESERVATION

Czaplewski states:

"A great field for ozone ventilation seems to open in the food industry, especially in the cold storage chambers of abattoirs. Ozone has been shown to have caused direct saving in many of these plants, the meat remaining fresh and sweet for a much longer period with ozone than without. In egg cold storage the ozone has given excellent results in that the disagreeable straw and box odors disappear, the eggs last longer, and fewer decay."

Bail<sup>1</sup> reports, referring to the Cologne abattoir:

"Meat that had decayed was at least partially reclaimed by the ozone, the mold coating having disappeared."

Saint Pére<sup>2</sup> states:

"Only pure ozone should be used in food preservation. Pure ozone on decomposition yields only pure oxygen, but this is not true of ozone contaminated with other gases. The latter gives a peculiar odor to eggs, meats, etc., due to the nitrogen oxide impurities. The odor fixes itself permanently in the

<sup>1</sup> Bail, *Prog. med. Wochenschr.*, 1913, No. 17, p. 217.

<sup>2</sup> St. Pére, *Revue Generale de Froid*, No. 34, March, 1912.

<sup>1</sup> *Gesundh. Ing.*, 1909, p. 498.

moist parts of meats, as the muscular fibers, ruining the best qualities. This contamination in ozone does not harmfully affect fruits; the thickness of the skin is apparently effectively increased, thus protecting it against the cold which otherwise hinders ripening."

For most varieties of foods there exists a certain critical temperature below which they may not be stored without injurious freezing and above which they are liable to deleterious bacterial invasion. It is extremely difficult to maintain rooms at the right temperature owing to the constant entrance and exit of operatives and because masses of material to be stored diffuse great quantities of heat on cooling down. The function of ozone is to limit bacterial activity at temperatures at which they might otherwise thrive.

**EGG STORAGE**—We have performed experiments with the preservation of eggs at ordinary temperatures and present the results herewith:

Preliminary tests were made to determine the effect of ozone on egg albumin and to note the effect of vacua on eggs. The eggs in all of the tests were from white Leghorn hens and were laid in the morning of the day of the tests.

The albumin of three eggs was well mixed, diluted with an equal quantity of water and divided into two parts. One part was put into a Petri dish, 6 inches in diameter and  $\frac{5}{8}$  inch deep and placed under a bell jar (9 inches in diameter by 12 inches high), with openings at the top and near the bottom at the side. Glass tubes provided with stopcocks were inserted through corks in these openings, the one passing through the top opening extending downward inside the bell jar almost to the Petri dish. The lower glass tube was connected to an aspirator and ozonized air containing 5 g. per cbm. was drawn from the upper tube over the Petri dish at the rate of 1 cbm. per hour. The total amount of air was 170 l., ozone 850 mg., period 10 minutes.

The albumin coagulated considerably and the whole mass turned a weak yellowish gray color which was distinctly noticeable but not pronounced. There was no odor of ozone in the resulting coagulum. Straining and weighing showed that the coagulum represented 27.4 per cent of the total albumin.

The remaining half of the albumin solution was treated in the same way with atmospheric air instead of ozonized air. The amount of air and the period were the same and there was 16.4 per cent coagulation but no discoloration.

Ten eggs were weighed, numbered and placed under the bell jar in a Petri dish. The jar was then evacuated to 0.46 mm. hg. and kept in this state for two hours, when the pressure had risen 2.37 mm. owing to evaporation from the eggs, none having broken. The air was then slowly introduced till atmospheric pressure was reached and the eggs removed and weighed.

Weight	1	2	3	4	5
G.	57.13	63.06	68.75	61.78	61.61
Loss, per cent.	0.402	0.365	0.465	0.461	0.372
Weight	6	7	8	9	10
G.	62.62	54.79	57.23	53.80	57.43
Loss, per cent.	0.335	0.381	0.540	0.473	0.400
Mean weight before	59.82 grams				
Mean weight after	59.57 grams				
Mean loss, g.	0.25				
Mean loss, per cent.	0.42				

These eggs were among the checks in the following experiments: Ten salt mouth bottles of 1 l. capacity were fitted with corks  $\frac{1}{2}$  inch thick, boiled in paraffine and provided with two glass tubes with stopcocks. Two eggs, weighed and numbered, were placed in each bottle and the corks replaced and sealed with paraffine. The bottles were exhausted to 0.59 mm. hg., after which air containing 320 mg. ozone per cbm. was slowly introduced. Ten control bottles were prepared in precisely the same way, with the exception that the air contained no ozone, and furnished with eggs. The bottles were numbered and put away in a dark room and at periods of ten days one ozonized bottle and one check bottle were opened and the eggs

examined and compared. One egg from each bottle was boiled and the other fried in Crisco and wherever possible all of the eggs were eaten. The temperature varied from 16° C. to 25° C. during the whole period.

Ten days—There was no ozone left in the bottle. Both eggs were all right in every respect; loss of weight, 0.10 per cent and 0.17 per cent.

The control eggs were all right; loss of weight 0.19 per cent and 0.24 per cent.

The remaining bottles were then evacuated and ozonized as at the beginning of the test and the control bottles evacuated and filled with air. In two bottles the eggs cracked and were discarded.

Twenty days—The ozonized eggs were all right in every respect; loss in weight, 0.45 per cent and 0.49 per cent; no ozone left.

Of the unozonized eggs the boiled one tasted like an old storage egg, but the fried one seemed all right; the bottle had no smell; loss in weight, 0.57 per cent and 0.56 per cent.

Thirty days—The ozonized eggs looked, smelled and tasted all right; no ozone left; spot in both shells because eggs had not been turned; loss in weight, 0.84 per cent and 0.55 per cent.

The unozonized bottle smelt from mildew; eggs looked weedy and spoiled; neither could be eaten; half of the inside of shell was black from lack of turning; loss in weight, 0.72 per cent and 0.75 per cent.

Forty days—Ozonized eggs both good in all respects; loss in weight, 0.65 per cent and 0.98 per cent; no ozone left.

The unozonized bottle smelt from mildew; both eggs thoroughly bad; could not be eaten; loss in weight, 0.88 per cent and 0.96 per cent.

Fifty days—Ozonized eggs both all right in all respects; no ozone; loss in weight, 1.25 per cent and 1.12 per cent.

Unozonized eggs essentially same as at 40 days.

Sixty days—Ozonized bottle showed slight trace of mildew; shells slightly mildewed; eggs both eaten but did not seem altogether fresh; loss in weight, 1.65 per cent and 1.52 per cent.

Unozonized eggs essentially as in 40 and 60 day test but more pronounced; loss in weight, 1.38 per cent and 1.76 per cent.

Seventy days—Smell of mildew in ozone bottle; boiled egg could not be eaten but fried egg was eaten and tested somewhat stale; loss in weight, 1.59 per cent and 1.69 per cent.

Unozonized eggs were thoroughly rotten and mildewed; strong H<sub>2</sub>S odor.

It should be noted that the corks were not tight after the first trial; the ozone disappeared in a short time, the period lessening after each treatment; the ozonized eggs lasted about twice as long as the unozonized eggs; the temperatures were very high throughout. Further test with ozone supplied constantly are to be reported later.

Fresh eggs are covered with a thin mucilaginous envelope which renders them air-tight, but after a time this dries and desquamates, leaving the porous shell unprotected. Then follows a period during which evaporation takes place and much of the water of the egg passes through the shell, being replaced by air from without. This air carries a variety of enzymes and other microorganisms through to the interior of the egg and it is probable that all the putrefactive changes in the egg are due to the activity of these organisms because the contents of fresh eggs are known to be absolutely sterile. Ozone by lessening the number and activity of these organisms inhibits the putrefactive processes to which stored eggs are otherwise liable.

#### CONCLUSIONS

From the evidence presented above, the following conclusions may be drawn:

I—Ozone destroys the odor of certain foodstuffs and other organic sources of odor.

II—Ozone is in no sense poisonous, though in great concentra-

tions it is capable of causing local irritation of the mucous membranes with which it comes in contact.

III—Prolonged ozonization is capable of ridding, at least in a measure, the atmosphere of food storage rooms of germ life, probably through rendering it an unsuitable medium for their support.

IV—Ozone is a valuable adjunct to ventilation, its function being the destruction of odor with consequent partial purification of the air; there is nothing either in the theory or in recorded experience to warrant its use for curtailing ventilation.

V—Eggs may be preserved longer with the aid of ozone than under similar conditions without.

VI—The analogy between laboratory tests and actual practical applications is often so obscure and replete with modifying factors that the extremest care must be exercised in applying the results of experimental observations to practice.

SPRAGUE ELECTRIC WORKS, BLOOMFIELD, N. J.

### THE IMPORTANCE OF ENZYMES AND ENZYME REACTIONS IN MEDICINE AND SURGERY<sup>1</sup>

By W. G. LYLE AND P. A. KOBER

We wish to present for your consideration this evening a brief review of the advances that have taken place in the methods of obtaining and identifying, for diagnostic purposes, some of the ferments present in the human body. These vary quantitatively so much, even under normal conditions, that only their absence, or marked diminution, is of importance in determining to what extent the organ itself is diseased.

We shall first discuss the digestive enzymes. Saliva contains a ferment called ptyalin, or better, salivary amylase. Its activities are restricted to the hydrolysis of the starches, converting them into maltose and a small amount of glucose. The ferment acts best in a slightly acid medium, strong mineral acids destroying it. Owing to the short time that food remains in the mouth, the amount of starch digested there is small. The ptyalin, after reaching the stomach, is destroyed by the hydrochloric acid present but many pieces of starch embedded in larger masses of food are protected from its action and may still undergo digestion, due to the action of the saliva swallowed with them. It is estimated that this starch digestion in the stomach may proceed for at least thirty minutes. In cases where the hydrochloric acid is low, or absent, pronounced digestion of starch will occur.

An interesting fact observed by Warfield and Koelker is that saliva contains another ferment, erepsin, which is capable of splitting some of the peptides to the amino acid stage. The reason for the presence of this enzyme in the mouth is not clear; however, it is probably of no digestive importance, being derived from the cells which line the ducts of the glands, from the mucous membrane of the mouth, and from the bacteria present there.

In the stomach we find the strong proteolytic enzyme pepsin, acting in an acid medium. Its function seems to be to break down the coarser colloidal particles into a non-coagulable state, preparatory to their further digestion by the enzymes of the upper intestinal tract. Peptic digestion of proteids in the stomach does not proceed as far as the formation of peptides and amino acids; on this fact is based a diagnostic test for cancer, known as the glycyI-tryptophan reaction. Theoretically, in the normal stomach, the di-peptid, glycyI-tryptophan, cannot be broken up into glycine and tryptophan by pepsin, whereas, if cancer is present this will take place. The tryptophan thus liberated is tested for with bromine. The splitting of this peptid may be due to an enzyme present in the carcinoma itself, or it may be brought about by the action of erepsin, a ferment widely distributed in the cells of the body, and undoubtedly secreted during the rapid proliferation and breaking down of the cancer cells. The practical difficulty with this test is that

there may be a regurgitation into the stomach of intestinal contents containing trypsin, which, of course, will split the peptid, and give the reaction, even if no carcinoma is present. For this reason the test has not proved satisfactory.

Pepsin and hydrochloric acid are absent in a disease of the stomach known as Achylia Gastrica, in which the mucous membrane becomes atrophied, and the glands do not secrete the ferment. The absence of pepsin and hydrochloric acid is also found in many cases of cancer of the stomach, and is a factor of diagnostic importance. It is interesting to note that in some cases where these are not present in the gastric contents, patients may go for years with apparently little digestive disturbance, as the protein is probably digested by the intestinal enzymes, thus showing the comparative unimportance of peptic digestion.

The pancreatic juice, which is poured out through a duct into the upper part of the small intestine known as the duodenum, continues the digestive process begun in the stomach, and breaks down the protein mass to the amino acid stage. Besides this proteolytic ferment called trypsin, the pancreas secretes a nuclease, an amylase, and a lipase. Owing to its deep retro-peritoneal position, and consequent difficulty in gaining any information as to its condition by palpation and methods available for other organs, the study of its ferments has been utilized as a diagnostic help in diseased conditions, the supposition being that if they were absent, or greatly diminished, either the ducts through which these were discharged into the small intestine were obstructed, or the gland itself seriously diseased.

Unfortunately, the amount of these ferments normally present is so variable, that unless they are completely absent or only traces of them found, great care must be taken in drawing conclusions as to the functional activity of the gland. However, cases have been reported by several observers where no ferments were found in the secretion of the upper intestine, and the diagnosis of an obstruction, or disease of the gland, was made, this afterwards being confirmed by operation or autopsy.

Great advances have been made in the study of these enzymes by the use of the duodenal tube. The apparatus consists of a thin rubber tube, a quarter of an inch in diameter, and 150 cm. in length. It is weighted at the end with an olive-shaped metal ball, perforated on the sides. The patient swallows this tube on retiring, and is given a glass of milk in the morning. After an hour the contents are aspirated, and tested for the presence of ferments. This has a great advantage over the stool examination method, as we are able to obtain the ferments in a fairly pure condition. The usual test for trypsin is the one recommended by Oscar Gross. This consists of a solution of one-half gram of casein dissolved in a liter of sodium carbonate (solution 1-1000). Duodenal contents are added to this casein solution, incubated for about eight hours, and then tested with a 1 per cent acetic acid. If the mixture is digested, showing the presence of the ferment, the solution will be clear; if no digestion has taken place, a precipitate is thrown down.

Other methods used for determining the presence of trypsin are the digestion of gelatin either in tubes or in plates, the digestion of fibrin, and of egg albumin.

Amylase is tested for by a method introduced by Wohlgemuth. He uses six small test tubes into which are put 5 cc. of a 1 per cent soluble starch solution. Tube 1 serves as a control; to the remaining five tubes are added 0.05, 0.25, 0.5 and 1.0 cc. of duodenal juice, diluted one-half with distilled water. The tubes are incubated for about thirty minutes and to each is added a drop of  $N/10$  iodine solution. The tube is selected as positive which shows an entire disappearance of all the blue color.

Lipase is best determined by incubating a mixture of the duodenal juice with triacetin for a given length of time, then titrating the acid formed in the usual way. It is necessary in doing this to run blanks.

As yet not a sufficient number of cases of pancreatic disease

<sup>1</sup> Presented at the New York Section of the A. C. S., Chemists' Club, June 5, 1914.



have been investigated, and the results correlated to the findings at operation and autopsy, to establish the value of these methods, on a firm diagnostic footing. But it is likely that with the development of better technique they will prove of great aid to the surgeon and physician in diagnosing these obscure conditions.

Before closing, we must mention some of the more recent clinical tests which are the direct result of enzyme investigations. 1—A method for determining urea quantitatively in the urine and blood. 2—A test for the diagnosis of pregnancy.

**UREASE**—Following the discovery of Takeuchi that the soya bean contains a urease, a method based on this observation has been developed for estimating the amount of urea in the urine and in the blood. The procedure is briefly as follows: A given quantity of the extract, or powder, of the dried soya bean is added to the material to be tested, and the ammonia which is formed from the urea is estimated in the usual way. The advantage of the test is that it is rapid and specific.

Abderhalden's test for pregnancy is based on the fact that foreign proteins circulating in the blood call out specific ferments which attack them. The test is as follows: A placenta, or after-birth, is ground up, washed free from all water-soluble material, and placed in a dialyzing bag with some serum from a suspected case. If the woman is pregnant, ferments specific for placental tissue are present in her serum. These will digest the placental tissue contained in the bag, and the dialysate will give the test for protein with ninhydrin, a reagent which gives a blue color with it. If she is not pregnant no ferments are present, and consequently the ninhydrin reaction is negative. A similar method is being tried for the diagnosis of cancer, using the cancer tissue instead of placenta, and dialyzing it with serum from the suspected case.

The fact that proteins introduced into the circulation other than through the intestinal tract are split up by ferments is of great importance in the study of anaphylaxis and in diseases like hay fever, urticaria, asthma and peculiar disturbances in the nervous control of the circulation. It seems that proteins taken through the mouth are split up by the digestive juices in such a way as to deprive them of their specificity, and

they are not absorbed until this has taken place. This would point to some regulating mechanism for preventing the re-absorption of heterogeneous albumin. It is probable that the feeding of excessive amounts of foreign proteins is responsible for the condition known as hives, for the disorders following the eating of shell fish and strawberries, and probably for some of the digestive disturbances found in infants fed on cow's milk. In hay fever, the continued absorption of proteins present in pollen, produces, in sensitized individuals, the well known symptoms of the disease.

Anaphylaxis, or in English, hypersensitiveness, is the opposite condition to protection. The word was coined to describe the peculiar effect which certain poisons possess of increasing, instead of diminishing, the sensitivity of the organism through their action. A hypersensitiveness occurs after the injection or absorption of a foreign proteid, and becomes manifest on the repetition of the injection. For example, if a guinea pig is injected with a given non-fatal amount of horse serum, and the injection repeated at regular intervals, after a time the animal develops an immunity, and is able to tolerate a dose much larger than the original one. Whereas, if an interval of time is allowed to elapse, say ten to fourteen days after the first injection, the second dose will produce a train of symptoms, in severe cases, characterized by great restlessness, rapid and labored breathing, collapse and death.

It is well known that some people are very susceptible to horse serum. This should be borne in mind if it is necessary to inject diphtheria antitoxin, as these very alarming and sometimes fatal anaphylactic phenomena occur, especially if the patient has had a previous, protective dose. In this connection it is interesting to note that some people are unable to ride behind a horse without attacks of sneezing, running of the eyes, etc. Some asthmatics who are sensitized to horse proteid have their attacks brought on in this manner.

This brief résumé suggests the great importance of ferment investigation in the practice of medicine and surgery.

HARRIMAN RESEARCH LABORATORY  
ROOSEVELT HOSPITAL, NEW YORK CITY

## OBITUARIES

### WILLIAM LOFLAND DUDLEY

On the morning of Tuesday, September 8, 1914, en route from Clifton Springs Sanitarium to his home on the Campus of Vanderbilt University in Nashville, Tennessee, William Lofland Dudley breathed his last after a sudden stroke of paralysis. During recent years, Dr. Dudley had been in poor health and his many friends became much concerned about him, especially when two years ago he retired from active participation in his professional, educational and sociological work.

Born April 16, 1859, in Covington, Kentucky, Dudley did not see the allotted three score years, but that part of his life following the attainment of his majority was full of hard work, enriched by good he did on every hand, and blessed with spontaneous affection from all those who enjoyed his friendship.

Prepared in the public schools of Covington, he entered the University of Cincinnati from which institution he was graduated in 1880 with the degree of Bachelor of Science. Last June he was the recipient of the degree of Doctor of Laws from his *alma mater*.

Dudley early exhibited his interest in chemistry, coming as a student under the influence of F. W. Clarke, then professor of physics and chemistry in the University. As a junior in college<sup>1</sup> he prepared a selenocyanate, an analogue of Buckton's double sulfo cyanate. While a senior under the direction of

Professor Clarke, he isolated a new volatile alkaloid, "spigelina," from *Spigelia marilandica*, or pink root.<sup>1</sup>

The youthful bachelor of science served as demonstrator of chemistry for one year in the Miami Medical College of Cincinnati during which time he worked out a modification of Böttger's subnitrate test for sugar<sup>2</sup> and a new test for gallic acid.<sup>3</sup> During the same time he published a work on the "Chemical Examination of Urine"<sup>4</sup> and a chart to be used by students in their study of urine. He at once became professor of chemistry and toxicology, in which capacity he served that institution for six years, when he resigned to accept the Chair of Chemistry in Vanderbilt University in Nashville, Tennessee. In 1885, Miami conferred upon him the honorary degree of Doctor of Medicine.

While at Miami he carried out an elaborate investigation on tobacco smoke, the poisonous principle of which he determined to be carbon monoxide.<sup>5</sup>

He was prominent among the music-loving people of Cincinnati, possessing a rich voice which charmed many in solos and ensemble

<sup>1</sup> "Preliminary Notice of a New Volatile Alkaloid," *J. Am. Chem. Soc.*, **1** (1879), 286; and *Am. Chem. J.*, **1**, 154-5.

<sup>2</sup> "Laboratory Notes on a Modification of Boettger's Test for Sugar," *Am. Chem. J.*, **2** (1880), 47.

<sup>3</sup> "A New Test for Gallic Acid," *Am. Chem. J.*, **2** (1880), 48.

<sup>4</sup> Broadside, Cincinnati (1880).

<sup>5</sup> "Poisonous Effects of Cigarette Smoking," *Medical News* (Philadelphia), **1883**, p. 53.

<sup>1</sup> With F. W. Clarke, "Some Selenocyanates," *Ber.*, **11** (1878), 1325.

at church and at charity concerts. He was a communicant of the Protestant Episcopal Church. He was ever active in civic affairs, being a commissioner of the Cincinnati Industrial Exposition from 1881 to 1885 and vice-president in 1884.

During this period he was retained by John Holland, the famous manufacturer of gold pens, giving much of his spare time to the investigation of iridium. He published a paper on the iridium industry<sup>1</sup> and one on Holland's method for melting iridium.<sup>2</sup> In a paper published in the Scientific Proceedings of the Ohio Mechanics' Institute, Jan., 1882, Dudley described his own contributions to Holland's process of making iridium points for gold pens. Holland found he could melt iridium by producing a phosphide. Dudley was able to remove the phosphorus afterwards by repeatedly heating the phosphide in lime. From this iridium he made incandescent electric filaments, which required no vacuum, and he also substituted this iridium for the negative terminal of an arc light.

The different status of teaching in a professional school and a university confronted him on moving to Vanderbilt. He carried into the academic life the knowledge of a man of affairs, who was a striking contrast to the be-cloistered student or the frocked pedagogue, especially characteristic of a denominational institution of that date. Such a teacher, one who taught and with rare power, one leading in movements for community welfare, one associating intimately with public men, a scholarly man of polish who moved among people with grace and without academic condescension or bland servility, possessing the more familiar characteristics of educationalists of today, was of tremendous influence, especially when that man remained the born aristocrat in his conceptions of honor and standards of integrity, but who at the same time was a democrat. He saw the needs of the middle southwest—and he set himself the task of meeting some of those needs. A powerful university was wanted in that city having more varieties of educational institutions than any other city of like size in our country. Practical men of education were needed to take hold of important places in the industrial development of the middle south and southwest which is rich in many ways, but even now not operating to the highest efficiency. He studied the professional status of various callings in that part of the country. He visited institutions of learning in the North, South and Europe. He spent vacation days seeing the industries where chemistry could help and was

a conscientious attendant at the meetings of the scientific societies and educational associations. As one result his students now occupy some of the most important technical positions within the range of the influence of Vanderbilt University.

Professor Dudley inaugurated courses in organic chemistry and in 1888 substituted manganese oxide for copper oxide in combustion methods of analyzing carbonaceous and hydrogenaceous substances.<sup>3</sup>

Professor Dudley began taking his students to visit industries that they might get a conception of chemical engineering. Among these was a black powder plant and the outcome of one of these visits was his description of the "Pierce Process for the Production of Charcoal, Wood Alcohol, and Acetic Acid," published in Hart's Journal.<sup>4</sup> It is a masterpiece of accurate

presentation, showing to scale in careful drawings many details of construction. I had the pleasure of being with him while gathering part of his data.

The problem of "delinting" cotton seed subsequently to be pressed for oil is one of great import to the southern part of our country and a problem to which many inventors have devoted much attention, the economic solution of which still promises a rich reward, for many million dollars worth of "de-lint" now goes to waste. Dudley with Perry secured U. S. Patent No. 344,951 for removing the lint chemically.<sup>5</sup> It depended upon treating the seed alternately with gaseous  $N_2O_3$  and  $SO_2$  and air. The process worked most satisfactorily on the laboratory scale, but never seems to have been tried out commercially. He was not much interested in commercializing once he had worked out his idea. He had sufficient means for his needs and no desire for wealth.

Later he completed a critical comparative study of the Roese and Allen-Marquardt<sup>6</sup> methods for the determination of fusel

oil which led to the conclusion that the latter is more accurate and more rapid. This study he utilized in his investigation<sup>7</sup> of the filtration of alcoholic liquids through wood charcoal, in which he concluded that oxidation plays no part in the removal of fusel oil. To him it was a case of adsorption.

<sup>1</sup>"Some Modifications of the Methods of Organic Analysis by Combustion," *Am. Chem. J.*, **10** (1888), 433 and *Ber. deut. chem. Ges.*, **21**, 3172.

<sup>2</sup>*J. Anal. Appl. Chem.*, **5**, (1891), 241.

<sup>3</sup>"Process for the Removal of the Lint from Cotton Seed," *J. Anal. Appl. Chem.*, **6** (1892), 140.

<sup>4</sup>"Notes on the Roese Method for the Determination of Fusel Oil and a Comparison of Results by the Allen-Marquardt Method," *J. Am. Chem. Soc.*, **30** (1908), 1271.

<sup>5</sup>"The Filtration of Alcoholic Liquids through Wood Charcoal," *J. Am. Chem. Soc.*, **30** (1908), 1784.



WILLIAM LOFLAND DUDLEY

<sup>1</sup>*Trans. Am. Inst. Min. Eng.*, **12**, 577.

<sup>2</sup>*Chem. News*, **45**, 168.

In 1908 he also completed an investigation on the influence of coal gas on the corrosion of wrought iron pipe laid under the streets in the city of Nashville, in which he came to the conclusion that coal gas had a retarding action.<sup>1</sup>

In his scientific work there is frequent evidence of the chemico-mineralogical influence of his distinguished teacher—and he himself shared in that compensation of the inspiring teacher in the work of his own students after they had left him. In 1880,<sup>2</sup> with Clarke, he described a new occurrence of graphite at the Ducktown Copper Mine and in 1890 he published an analysis and description of a curious occurrence of vivianite, which was made up of plant roots, 1 cm. in diameter and up to 400 cm. in length, entirely replaced by hydrated iron and aluminum phosphate.<sup>3</sup>

Not infrequently Dudley harked back to his work with Holland and the elements of the eighth group. He showed that platinum black is soluble in dilute hydrochloric acid, but only when oxygen is present.<sup>4</sup> He worked on the electro-deposition of iridium<sup>5</sup> and showed that iridic hydrate,  $\text{Ir}(\text{OH})_3$ , suspended in bags would serve to keep the bath of uniform composition. This was later independently determined by Wahl, who graciously acknowledged Dudley's priority, the delay of publication of whose work was due to professional obligations.

In 1896 he prepared and described nickelo-nickelic hydrate,<sup>6</sup>  $\text{Ni}_3\text{O}_4 \cdot 2\text{H}_2\text{O}$ . Later<sup>7</sup> he gave an account of further work on the "Action of Fused Sodium Dioxide on Metals," describing a ferric hydrate,  $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ , which was magnetic, and a hydrated platinum sesquioxide,  $\text{Pt}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ . His last published scientific work, and perhaps his most important in the field of pure inorganic chemistry, was with E. V. Jones on a "Spectrographic Study of Tellurium," in which he found little evidence of the oft-suspected complexity of that chemical element of today.<sup>8</sup>

Professor Dudley made no great contribution to the theories of chemistry. Few are they that do. However, for years he sought a relation of the color transmitted by thin films of metallic elements and that emitted by their incandescent vapors, but was unable to associate them to his satisfaction, although many new data were presented in the paper published in 1892.<sup>9</sup> I had the pleasure, as a graduate student, of assisting him in part of this work. From a long and critical study of the relationship of the heat of vaporization of gases to their density and also their boiling points,<sup>10</sup> he enunciated the following law:

"In any homologous series, the heat of vaporization in a unit of volume of the vapor, under the same conditions as to temperature and pressure, is proportional to the density and also to the absolute boiling point."<sup>11</sup>

In an official capacity he attended the opening of the Kent Chemical Laboratory of the University of Chicago, which marked a prominent forward movement in the development of our science in this country, and reported the proceedings for our Society.<sup>12</sup>

At that time his own chemical laboratory occupied the entire ground floor of the large Vanderbilt Hall. A bequest from the

<sup>1</sup> "Effect of Coal Gas on the Corrosion of Wrought Iron Pipe Buried in the Earth," *J. Am. Chem. Soc.*, **30** (1908), 247 and *Progressive Age*, **26** (1908), 137.

<sup>2</sup> "Graphite from Ducktown, Tenn.," *Am. Chem. J.*, **2** (1880), 331.

<sup>3</sup> "A Curious Occurrence of Vivianite," *Am. J. Sci.*, N. S., **40** (1890), 120.

<sup>4</sup> "The Action of Gaseous Hydrochloric Acid and Oxygen on the Platinum Metals," *J. Am. Chem. Soc.*, **15** (1893), 272.

<sup>5</sup> "The Electro-deposition of Iridium, a Method of Maintaining the Uniform Composition of an Electroplating Bath without the Use of an Anode," *J. Am. Chem. Soc.*, **15** (1893), 274.

<sup>6</sup> *J. Am. Chem. Soc.*, **18** (1896), 901.

<sup>7</sup> *Am. Chem. J.*, **23** (1902), 59.

<sup>8</sup> *J. Am. Chem. Soc.*, **34** (1912), 995.

<sup>9</sup> "The Colors and Absorption Spectra of Thin Metallic Films and of Incandescent Vapors of the Metals, with Some Observations on Electrical Volatility," *Am. Chem. J.*, **14** (1892), 185.

<sup>10</sup> *J. Am. Chem. Soc.*, **17** (1895), 969.

<sup>11</sup> *Ibid.*, **16** (1894), 213.

Furman estate was intended for a new laboratory, but the estate was long involved in litigation. Vanderbilt Hall was destroyed by fire and in time the legal controversy was decided in favor of the University. From the quarter of a million dollars thus made available Professor Dudley designed Furman Hall, the new laboratory which was built about ten years ago. He was not satisfied with the various kinds of flooring then in use, so set about designing a composition flooring which, in the opinion of the writer, is one of the most satisfactory materials for the construction of floors known today.<sup>1</sup> His patent (U. S. Pat. No. 839,829 of 1906) covered a magnesia-cement composition containing cellulose water-proofed with paraffin and asbestos. It was offered by friends to a number of composition flooring concerns, but never taken up by them. No doubt his patent has been infringed, but he could not be persuaded to prosecute. "I'd like them to be decent, but what's the use of a nasty fight? I have my laboratory floor and it's what I wanted." He preferred peace, but there was no honorable length to which he would not go, when once he entered a contest.

Professor Dudley lectured fluently and easily, yet with forceful clarity. His lectures were abundantly illustrated, many demonstrations being devised by him but never published, although *Science* printed a short note from him on a neon tube.<sup>2</sup> He described a most satisfactory down-draft<sup>3</sup> which he devised for his lecture table and which may well be patterned after by others.

Professor Dudley and Kirkland were intimate friends and messed together before the latter married. Dr. Dudley never married. After Dr. Kirkland became Chancellor of the University he called upon Dr. Dudley in many ways, among them to assume the deanship of the medical school and thoroughly reorganize it, as Dudley had urged. This extra labor was begun in 1895 and continued to his retirement. New buildings were designed and equipped; a strong faculty was brought together; the standard was raised and the number of students increased until the medical college of Vanderbilt ranked in the first class of medical schools.

During the first few years of this extra work he also undertook the direction of affairs of the Tennessee Centennial Exposition of 1897 and handled it with such care that no deficit appeared at its end, an unusual condition for such undertakings.

These and other civic duties caused him to sacrifice his music, though he maintained constant interest in all forms of art and literature, being an active member of the select and famous Round Table and The Oaks of Nashville.

Dr. Dudley never seemed in a hurry, but he was always on time. He possessed an even temperament that was most difficult to ruffle, yet he was not unfamiliar with righteous indignation. When he espoused a cause, he was unflinchingly persistent in its prosecution. He did not recognize such a thing as failure. He had much to do with the legal contest between the Board of Trustees of the University and the Methodist Episcopal Church South concerning the gift of Mr. Carnegie. The Trustees, Chancellor Kirkland and Dr. Dudley won eventually and the medical school increased its endowment a million dollars thereby.

Thrown back into a field where he began his teaching he renewed his interest in the applications of physical science to medicine. Right after Röntgen's announcement he persuaded his colleague, Professor Daniel, to radiograph his (Dudley's) head. One of the results observed was the whitening of Dudley's hair nearest the Crookes tube. He was, therefore, the discoverer, or if not the discoverer, one of the first and an independent observer, of some of the physiological effects of X-rays.

When he went to Vanderbilt, Dr. Dudley organized an athletic association because of his love for clean sport and clean sportsmanship. In resolutions recently passed that Association said:

"He had a wider and a more intimate acquaintance with the

<sup>1</sup> *Proc. Eng. Assoc. of the South*, **18** (1907), 3.

<sup>2</sup> "Neon and Electric Waves," *Science*, New Series, **30** (1909), 525.

<sup>3</sup> *J. Am. Chem. Soc.*, **30** (1908), 973.



students and alumni of Vanderbilt University than any other person; he was loved by all of them, and that was his sufficient compensation."

The Vanderbilt athletic field is called "Dudley Field." He extended his influence to students of other institutions by organizing the Southern Intercollegiate Athletic Association about twenty years ago. It became very powerful and he was its president up to two years ago. He was a member of the Executive Committee of the National Intercollegiate Athletic Association and an active member of the Football Rules Committee which brought about many reforms in the modern American game. He organized the University Club of Nashville and was its president through the trying years. He had many interests in students' affairs, being grand consul of the Sigma Chi fraternity (1897-9). Dr. Dudley had collected a very large and valuable scientific library, which he left to Vanderbilt University.

His recognized administrative ability brought him offers in executive positions in other institutions, but he preferred to remain at Vanderbilt with the upbuilding of which he had had so much to do.

He was a loyal member of the American Chemical Society (since 1890), urging all his graduates to become members. He served the Society in many ways, organizing the Nashville Section and being a Councillor-at-large when he died. He was an active fellow in the American Association for the Advancement of Science, especially "Section C" before the Chemical Society became active. He was secretary (1888) and then chair-

man of Section C (1889), his retiring address being a splendid presentation of an extensive study of the nature of amalgams.<sup>1</sup> He was a Fellow of the London Chemical Society (since 1890), a Member of the German Chemical Society, the Society of Chemical Industry (since 1887), American Electro-chemical Society, and others. He was secretary of the section of inorganic chemistry at the International Congress of Arts and Sciences in St. Louis in 1904.

He was an United States Commissioner to the Seventh International Congress of Applied Chemistry, member of the Executive Committee and Vice-Chairman of the Section on Law and Legislation of the Eighth Congress. He, as other members of that committee, took long trips to New York and did much towards making that Congress successful.

He long ago became a non-resident member of the Chemists' Club<sup>2</sup> and fathered the splendid paper about the Club which was presented at the Cincinnati meeting of the Chemical Society<sup>3</sup> and later appeared in *THIS JOURNAL*.

This is only a part of the life-story of a good man, whose intimate friendship I was privileged to share a quarter of a century. He had many intimates, who loved him. He was a man whom men loved. The influence of such a man goes on through generations. He was noble in all that is associated with a gentleman and now rests with his forebears in the place of his birth.

CHARLES BASKERVILLE

COLLEGE OF THE CITY OF NEW YORK  
September 21, 1914

## CURRENT INDUSTRIAL NEWS

By M. L. HAMLIN

### SOME PHASES OF THE INDUSTRIAL SITUATION IN GREAT BRITAIN

The European war has created such unprecedented conditions in the foreign industrial world that all other factors fade into insignificance, and because of the tremendous recent changes even the latest news before the development of general hostilities is entirely out of date. Since the beginning of the war German periodicals have been stopped and there is practically no news directly from the continent, but the English journals give a complete and accurate description of the conditions existing there. In a long editorial *Engineering* (London) says in part [98 (Aug. 21, 1914), 253] after praising the course of the government:

The Commercial Intelligence Branch of the Board of Trade have done well to offer guidance and help by emphasizing the importance of prompt and vigorous propagandism, in order to extend our markets by the taking of every legitimate means of utilizing the opportunity presented by the cessation of exports from Germany and Austria-Hungary, particularly to our Colonies. The total exports from Germany during the six years ended 1912 increased from 312<sup>3</sup>/<sub>4</sub> to 440<sup>1</sup>/<sub>2</sub> million sterling (1 l. sterling = \$4.86). If we take only manufactured articles, we find the increase is from 211 to 284<sup>1</sup>/<sub>2</sub> million, while in iron and steel and manufactures thereof the advance has been from 35<sup>3</sup>/<sub>4</sub> million to 60 million sterling, and of machinery, including locomotives and boilers, from 17.3 to 34.8 million sterling. In 1912 Germany's exports of electrical appliances and apparatus exceeded 8 million sterling. Of dynamos, our exports in 1913 were 2,269,000 l., whereas Germany's total in 1912 was 2,521,000 l. In the case of electric glow-lamps the disparity is enormous, the exports from Britain being 152,500 l., as compared with 2,447,000 l. from Germany. And so it is throughout practically the whole range of electrical industry. In this respect alone, it will be seen that there is a great field for British endeavour. The textile industry is one of very great consequence, even to engineers by reason of its machinery requirements, and it is found, for instance, that while our exports of cotton stockings and socks

in 1913 totalled only 199,000 l., those from Germany totalled 3,319,000 l. in 1912, the last year for which German export statistics are available. The United States, Argentina, France, and almost all countries in the world have been captured by Germany. Of woolen and worsted piece goods Germany's exports totalled 13<sup>1</sup>/<sub>2</sub> million, and here Canada, Australia, Argentina, Japan, and British India, in the order named, account for a very considerable part of the total. In respect of cutlery our exports were 836,000 l., whereas Germany's were 1,747,800 l.—double our total. In the case of iron and steel wire our exports totalled 1,058,100 l., and Germany's 3,176,000 l., or three times our total. Of enamelled hollow-ware, etc., our exports were only 531,000 l., and those of Germany 1,776,000 l.—again more than a threefold total.

The great disparity which is brought out by these Government returns of the British and German exports serves to illustrate clearly the efficiency of Germany from a commercial and industrial point of view. No one can for a single moment have doubted this efficiency, or the keenness with which commerce, particularly overseas commerce, has been pursued by the people of Germany. Time and again we have enforced this, and have sought to point the moral. Consequently there can be no base motive attributable to us in again directing attention to this question. We have contended that if we are to fight Germany in neutral markets we must adopt the German methods so far as these are essential. In the great majority of cases the superiority of our products has been recognized, but less durable and cheaper goods are obtainable from other countries. This is a fault of our qualities. In iron and steel wire, where the German exports are treble those of Britain, the same holds good. In the interior of Africa and in the uplands of Australia, the purchasers of fencing-wire, whether plain or barbed, do not think that any advantage is to be gained by the superior and climate-resisting qualities of the British wires,<sup>4</sup> except where they are in use close

<sup>1</sup> *Proc. A. A. S.*, **38** (1889), 149.

<sup>2</sup> Mr. Berolzheimer, the Librarian of the Club, kindly collected the bibliography here used.

<sup>3</sup> *THIS JOURNAL*, **6** (1914), 407.

to the seaboard, so that the black wire is often preferred to galvanized wire. Thus, as our Trade Commissioner in New Zealand points out, practically any wire will last under such conditions, and people want the cheapest. The same applies throughout the whole gamut of manufactures, and the time has probably arrived when in this, as in other matters, the British manufacturer must be prepared to meet the wishes of the client. We would, however, be false to ourselves as a nation if we assumed a superiority throughout the whole field of manufactures. It is right that we should be fair to Germany. The producers of that country who have taken up new industries have profited by a study of our appliances, and, in some cases, have succeeded in achieving greater economy in production with equality in efficiency. They are therefore able to underbid us in some manufactures, assisted as they are also by the procedure of sending to foreign countries, and to Britain even, the surplus productions of their factories, against which there is not debited either establishment charges or profit. Moreover, wages are lower, hours of labor longer, and idle time less, so that, with the same, or as good, plant, the cost of production is lessened.

There are many respects in which our producers do not sufficiently closely study the particular needs of clients. We have persistently advocated that designers in engineering structures ought to utilize as far as possible standard practice, and it must be admitted that there is a sufficient range, for instance, in sections of steel bars and beams to meet all requirements. But in details we show great reluctance in meeting the specified needs of the prospective purchasers of our manufactures.

Another important consideration is the representation of British firms in neutral markets; in this respect the Germans have offered an example which ought to be very carefully considered. The agencies for engineering firms ought to be in the hands of trained engineers, so that a maximum of information may be obtainable and the fullest measure of compliance with requirements assured. The Germans have made a special feature of quoting "ex-warehouse," which includes all duty and port dues. These efforts towards simplifying purchase operations by clients in colonial and foreign markets are of incalculable advantage, and those who conform to them invariably profit immensely. They involve, we admit, a certain measure of intelligence and care in the commercial departments of our industrial establishments, but we are convinced that with the extension of commercial education, the requisite posts can be filled by capable men, with immense advantage to the export trade of the firm and of the country.

The State has also a duty in this matter of increasing the area of British markets. The Commercial Intelligence Department of the Board of Trade, who are undertaking the new campaign, have done useful service in the recent past, and they will, we doubt not, increase their efforts. But much more can be done, particularly in the ensurance of favorable conditions for transport and for a greater measure of financial assistance in co-operation with the British and Colonial banks. On former occasions (see *Engineering*, 92, 801) we have referred to the assistance rendered by the more liberal banking conditions in Germany, and we see no reason why similar help should not be given by our banking and financial institutions in connection with the foreign and colonial work of our industrial firms. Britain has awakened from a state of complacency in many matters, and we hope that one result will be that the banks will, without in any way jeopardizing that safety which is so pronounced a feature of their organization, see their way to give more liberal consideration to what is, after all, a safe speculative business—the promotion of export business on easy terms. Regarding transport, we regret that some of the shipping companies are dealing very hardly by the shippers, especially at the present juncture. Had the British Navy not maintained the command of the sea, and had the British Government failed to insure war

risks by direct financial help, there might have been some reason for heavy freight charges at the present moment; but war risks having been minimized or greatly reduced, the duty of the shipowner to-day is to cast in his lot with all who are doing everything in their power to maintain normal industrial conditions.

#### FINANCIAL RESOURCES

England's financial resources are one of the most important if not the most important factors in her position. A new book which has received considerable favorable criticism, "The Industrial History of Modern England," by G. H. Ferris, has many interesting data on this subject. The author states that the total capital of the United Kingdom is broadly estimated at \$15,000,000,000. He continues:

According to the report of the Census of Production, first taken for the year 1907, only about a tenth of the whole consists of manufacturing capital, including the value of lands and buildings; and it is remarkable that this capital is equal only to two years' net output of industrial business (not including cost of materials or transport).

On the other hand, Sir George Paish estimates the amount of British capital invested abroad at £3,500,000,000, or more than twice as much as the capital engaged in home manufacture. The total annual income of the country is put at about £2,000,000,000. This appears to be shared and contributed, approximately, in the following proportions:

Industrial production (net).....	£760,000,000
Agriculture and fisheries.....	£220,000,000
Distribution.....	£400,000,000
Professional, governmental, and other services.....	£350,000,000
From foreign investments and services (coming in, largely as imported materials).....	£240,000,000

Perhaps the most remarkable fact of all is the increasing part which foreign investments play in the budget of the British people. Their amount is increased by £100,000,000 a year; and the income from them is estimated at from £140,000,000 to £170,000,000, which is equal to two-sevenths of the sum brought under review of the Inland Revenue Department as income, properly so called, from business concerns, professions, and private employments at home.

British exports, which had stood at £180,000,000 in 1867 and £190,000,000 in 1869, rose in the first year of the [Franco-Prussian] war to £199,000,000, then to £223,000,000 and in 1872 to a maximum of £256,000,000; in 1873, when France paid her indemnity of £200,000,000, and, for the rest, was kept busy restoring the public and private property that had been destroyed, this maximum was maintained.

But the loss of two competitors now proved itself to be also, the loss of two consumers. The two countries had sacrificed to their ambitions nearly 200,000 able-bodied combatants killed, and a larger number wounded. France had now to pay the money penalty—that is, had to enter upon an arrangement by which a sum of about £8,000,000 was to be paid yearly in perpetuity, or till the capital debt was redeemed.

Germany had to learn that a victory may be only a degree less costly than a defeat. Much poorer than France in hoarded wealth, she had been deprived for many months of the labor of a million of her stoutest men. With the return of the armies, this labor-force was suddenly restored, not to a normal activity, but in a feverish effort to recover lost ground.

The expenditure of the French milliards—chiefly on railways, other public works, and armaments—created a class of manufacturers and workers which was to be, in future years, dependent on Government favors, and led to a rage of industrial speculation. In five years the number of joint-stock companies increased nearly fivefold. There being no corresponding increase of the power of consumption—because, while the French indemnity may be said to have paid for the maintenance of the German armies, it did not and could not compensate for the



arrest of wealth-making during the war—an acute reaction took place in 1874; and serious depression continued until 1879, almost every branch of German industry being affected.

Between the two years named, British exports declined from £239,000,000 to the minimum of £191,000,000, rising again to £241,000,000 in 1882, and then once more falling. Austria, always bound economically to Germany much more closely than England is, received a still more severe shock.

The mischief of warfare is comparatively easy to appreciate. It destroys capital and labor at once; it destroys past wealth, present wealth, and the means of creating wealth in the future. It thus compels more strenuous labor on the part of a weakened community, and at the same time compels abstinence—that is, it reduces the power of consumption from which alone the demand for labor can arise.

#### THE LABOR SITUATION

The general temper both among employers and employees is indicated in many typical news items. *The Engineer* (London), 98 (1914), 251, says that labor disputes are subsiding; settlements of three disputes were arrived at by the joint sub-committee of the Welsh Conciliation Board, at an adjourned meeting at Cardiff. These disputes affected over 3500 men, who had been rendered idle. The object in view is to eliminate all labor troubles from the South Wales coal field during the war. Hopes are entertained that other disputes may be satisfactorily disposed of; the trouble at the Faldan colliery was settled on Monday.

In a letter to the district committees (printed, *Ibid.*, p. 247), Mr. J. T. Brownlie, the chairman of the Amalgamated Society of Engineers, and Mr. Robert Young, the general secretary, make the following statement: "In view of the fact that the nation is involved in war with European Powers, the executive council have had under consideration a request from the Employers' Federation, due to pressure being brought to bear by the Government, for the completion of vessels required by the Admiralty, and all ordnance work necessary for the nation's requirements. As this undoubtedly has special reference to the working of overtime, the council have given serious consideration to the matter, and to all that is involved therein, and hereby request that district committees shall instruct our members to work the overtime necessary under the circumstances."

The condition of the labor market has of course been markedly affected, and some works have been compelled to shut down on account of the shortage of labor. According to the *Jour. of Gas Lighting and Water Sup.*, 127 (1914), 380, Mr. John S. Ineson, the Engineer and Secretary of the Ventnor Gas and Water Company, has written that (except the foreman) every man on the works—stokers, yardmen, and laborers—has been called up to serve in the Navy and Army Reserves as well as in the Territorial Force. By the second and third of August every man had left; and there are now on the office staff only the collector and the office boy. The gas and water works and the reservoirs are under the protection of the military. Mr. Ineson doubts whether there is another company so severely affected as his has been.

Again from *Engineering* we learn that the agricultural Consultative Committee, appointed by the President of the Board of Agriculture, issued a statement in relation to the shortage of harvest labor owing to mobilization. The committee announce that active steps are being taken to supply the deficiency, by means of special instructions issued to the Labor Exchanges. The committee appeal to landowners to facilitate the employment of members of their estate staffs, such as keepers and woodmen, on neighboring farms. Further, the committee have accepted a timely offer from the Boy Scouts' Association to use scouts in the conveyance of messages between farmers and possible sources of labor, and they record the fact that local scouts are being encouraged to assist farmers in their respective

neighborhoods. Scouts, it is added, are entitled to receive fair remuneration for their work.

The situation has not redounded to the disadvantage of all trades and classes, for the *Yorkshire Post* writes with evident satisfaction: "It will be good news to the many thousands of clothing operatives in Leeds, and to citizens generally, that this district—the most important clothing center in the kingdom—is likely to share in the Government orders for Navy and Army clothing. A local firm of wholesale clothiers, accustomed to this particular class of work, have been asked to place their factory at the disposal of the Government, which means that other work which they are therefore unable to undertake will be distributed among other houses. A week or two, however, must elapse before activity can become general. The khaki has to be manufactured—largely in the Leeds, Dewsbury, and Batley districts, where some mills are now working full time—and until deliveries of the piece goods are made little can be done at the clothing factories. The Government supplies the whole of the materials; all that the clothing factories have to do is to make them up, and everything has to be carried out strictly according to Government specifications. Only a limited number of firms who make a specialty of the work are on the recognized Government list, and, of course, when they are busily employed thus, the ordinary trade must be done by others." And the workmen at the famous Yarrow yards may benefit, for it is announced that if the firm are fully satisfied with the speed of completion, when the last of the three new destroyers, *Miranda*, *Minos*, and *Manly*, on which their men are working night and day and on Sundays, has been handed over, 1000*l.* (nearly \$5,000) will be distributed among the leading hands and others.

#### THE PATENT SITUATION

The new patent legislation, both the enacted and projected laws, and the reasons which in the eyes of the Government necessitated the passing of these laws, are commented on at some length in *London Engineering*, 98 (1914), 280. According to this journal, the number of British patents granted annually to Germans and Austrians is very large. In the last annual report issued by the Comptroller-General of Patents, the numbers were as follows:

Total number of patents granted.....	16, 154
Number granted to Britons.....	8, 263
Number granted to Germans.....	2, 606

From the latest particulars as to the number of patents granted annually in Germany it would seem that of 13,080 patents granted in one year, 8831 were granted to Germans and only 749 to Britons. It will thus be seen that the percentages are very different.

A cry is raised periodically as to the hardships that are caused to British labor by foreign patentees who work their inventions abroad, to the benefit of their own labor markets, and import, free of duty, their products into this country.

Now we are confronted with the proposal that all patents granted in this country to alien enemies should be forthwith revoked. The proposition seems attractive, but there is, as we have pointed out, a large patent property in Germany which belongs to British inventors. If we revoke all the patents belonging to the subjects of the States with which we are at war, we must expect that the Governments of those States will act in a similar manner as regards the patents held by us. Our gain would then be a good deal counterbalanced.

The Government do not propose any drastic measures, but have taken certain steps for the protection of British trade, and to that end have passed an Act (Patents, Designs, and Trade Marks (Temporary Rules) Act, 1914) amending the Patents and Designs Act, 1907, and the Trade Marks Act, 1905, in a certain manner, and have taken power to make rules and to do such things as they think expedient for avoiding or suspending, in whole or in part, any patent or license granted to, and the



registration of any trade mark the proprietor whereof is a subject of any State at war with His Majesty. The Board of Trade has set up the necessary machinery to carry out the Act, and has issued rules from which it appears that they may, on the application of any person, and subject to such terms and conditions, if any, as they may think fit, order the avoidance or suspension of the rights of patent and registers of trade-marks of aliens. The Board, before granting any such application, may require to be satisfied on three points.

The first point of which the Board will require to be satisfied is that the patentee, licensee, or proprietor is the subject of a State at war with His Majesty. This point looks very simple and easy of proof, but when the time comes, it may raise difficulties that are not apparent to those who are not well posted as to the preparations of our enemies.

The second point requiring proof is that the person applying intends to manufacture the patented article, or to carry on the patented process, or intends to manufacture the goods in respect of which trade mark is granted. We cannot say what sort of proof the Board will require on this point, but it, and the third point, are evidently intended to prevent applications under the Act by persons who have no interest.

The third point on which the Board will require to be satisfied is that it is in the general interests of the country or of a section of the community or of a trade, that such article should be manufactured, or such process carried on, or the registration of the trade mark avoided or suspended.

The Act and Rules made under the new Act are to continue in force only during the continuance of the present state of war in Europe and for a period of six months thereafter. This provision raises an interesting question. Are patents, designs, and trade marks to be avoided or suspended for not longer than six months after the termination of the war, and then to be automatically restored, or is the avoidance or suspension to be irrevocable? Evidently the latter is not to be the case, for the Board of Trade have powers to revoke any avoidance or suspension at any time in their absolute discretion. The matter appears to us to be in a state of confusion, and the Government has evidently found it to be so, for the President of the Board of Trade introduced a Bill into the House of Commons to amend the Patents Act they passed only a few days previously. The President in his introductory remarks explained that the new Act was not as clear as it might have been.

#### THE IRON AND STEEL TRADE

Manufacturers are beginning to find that the decline in activity is not nearly so sharp as they were led to expect, though it is entirely possible that by the time this is published, some new turn of the situation will have changed this. According to *London Engineering* (98, 276 August 28, 1914), while "the condition of affairs in the malleable-iron trade in the west of Scotland is most satisfactory and makers are very busy, business in the Scotch steel trade has been rather a serious problem to the different managements for a long time back, and the newer phase is also one requiring careful handling. During the past week the outlook has improved considerably, as shipping facilities are more favorable, but heavier freights and increased costs for raw material are all against buyers, who are still somewhat backward to fix up contracts. The mails from abroad are bringing in very satisfactory inquiries and orders from markets which have remained loyal to the Scotch makers, and those which in recent years purchased large quantities of steel material from the Continent will now require to pass their business here or else to America."

#### ALLOY-STEEL GEARS IN MACHINE TOOLS

The issue of *Machinery*, for August of this year, says that alloy steels, such as chrome-vanadium and chrome-nickel,

have been used with more or less success for gears in machine-tool construction. One machine-tool builder in the Middle-West has tried both these alloys for gears; very unsatisfactory results were obtained, and he has gone back to ordinary carbon steel, having a carbon content of 0.20 per cent, heat-treating the steel in the most scientific manner known. The article states that with special alloy steels the limits of fluctuation in the heat treatment are much narrower than in ordinary carbon steel, and the material must be handled much more carefully if good results are to be expected. Since using carbon steel the machine-tool builder in question has found that his troubles in the way of breakage and stripping of gear-teeth are practically eliminated.

#### THE UNITED STATES COAL OUTPUT

The *Iron Age* states that the coal output in the United States for the year 1913 has again broken all previous records. The figure given by our contemporary is 570,048,125 net tons, or considerably more than double the output of 1900, and more than eight times that of 1880. The value of the coal mined in 1913 is given as \$760,488,785. Compared with the year 1912, the output for 1913 shows an increase of 35,581,545 tons, or nearly 7 per cent. Pennsylvania mined more coal in 1913, both anthracite and bituminous, than in any previous year in the record of the industry. The output reached 265,306,139 tons, of which 91,524,927 tons was anthracite and 173,781,212 tons bituminous.

#### BY-PRODUCT COKE OVENS IN RUSSIA

The United States Consul at Odessa reports that there are in South Russia ten plants owned by nine firms for the production and utilization of coke by-products. In the first nine months of 1913 these firms were operating 887 coke ovens producing by-products, besides a large number of the old type. The increase in the last four years in these ovens was 563, or 15.8 per cent. In 1912 5,689,411 tons of coal were consumed to produce 4,252,697 tons of coke, as compared with 2,774,733 tons of coal to produce 2,020,831 tons of coke in 1903. Sulfate of ammonia is beginning to be used in Russia as a fertilizer; but most of it is still exported. The pitch is used mainly, if not exclusively, for the production of briquettes, and the heavy oils for the impregnation of railroad sleepers.

#### ON ACCUMULATOR ELECTROLYTES

The July issue of the Proceedings of the Société Belge des Électriciens states that most of the patents taken out in those countries where there is no preliminary examination cover re-inventions, not genuine inventions. This is due to the fact that the majority of researchers explore fields which are not familiar to them and neglect to inform themselves thoroughly on all points. According to our contemporary, this state of matters prevails in the construction of electric accumulators more than in any other branch of industry. The immobilization of the electrolyte, for example, constantly gives rise to a number of patents dealing with processes, some of which have been known for the last thirty years or more.

#### THE FULLAGAR INTERNAL COMBUSTION ENGINE

A gas engine of such novel type and combining many new features was recently demonstrated at a joint meeting of the Institutions of Naval Engineers and Shipbuilders at Newcastle-upon-Tyne, that it is worthy of a fairly extensive description.

Three fundamental factors are chiefly responsible for the difficulties in the construction of internal combustion engines of existing types. These factors are: (a) That the heat per unit of surface radiated by the flame to the cylinder walls increases with the size of the cylinder, while the thickness of metal through

which this heat has to reach the cooling water also increases; (b) that the weight per horse-power increases with the size of the cylinder; (c) that useless forces are called into play—useless in that they are either stationary and do no work or even produce negative work. These result from (1) the fluid pressure on the cylinder covers, which has to be transmitted through the framing of the engine; (2) the negative work of the compression stroke, which in single-acting engines produces a reversal of twist in the crankshaft; and (3) the inertia forces resulting from want of balance, and imperfect cushioning. The Fullagar internal combustion engine eliminates these factors, and has besides the advantages of mechanical simplicity and accessibility.

The construction, which is shown diagrammatically in Figs. 1 and 2, consists in using as a unit two open-ended cylinders side by side, each with two pistons, and rigidly connecting the

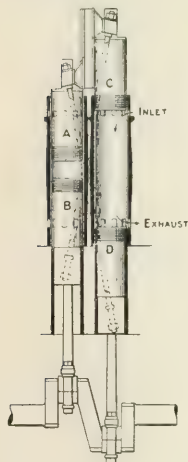


FIG. 1

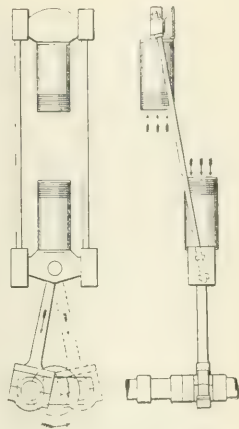


FIG. 2

pistons A to D, and C to B, by means of pairs of oblique rods, external to the cylinders. The action of the engine is as follows: An explosion taking place between A and B drives B down and A up, drawing up D by the oblique rods, and giving, through the two connecting-rods, two equal and opposite impulses to the two cranks. The side thrust produced by the oblique pull is, of course, taken by the crossheads of A and D, which are provided with suitable guides for the purpose. The obliquity of the rods is small, less than the maximum obliquity of the connecting-rods, so that the friction is actually less than would be the case if each piston had its own crank and connecting-rod and the mechanical efficiency of the engine is high. At the ends of their strokes the pistons uncover inlet and exhaust ports in the cylinder walls, as in the Oechelhäuser arrangement. The engine works on the two-stroke cycle, and each crank receives, therefore, two impulses per revolution. Air is supplied

to the cylinders by low-pressure air-pumps, which can be driven from the engine by side levers in the ordinary way.

It will at once be clear that with this construction useless forces are avoided or greatly reduced. There are no cylinder covers or, in fact, any high-pressure joints in the engine. There are no vertical stresses on the framing of the engine at all. The pressure of the explosion is entirely taken between steel parts—namely, the cross-head, oblique rods, connecting-rods, and crankshaft; and only the secondary reactions of the slippers, from one-fifth to one-twentieth of the explosion forces, reach in a horizontal direction the framing of the engine. The fluid pressure in each cylinder acts at every moment equally on the two cranks. The main bearings are thus relieved of practically all load, except for the weight of the parts which, acting vertically, is just sufficient to keep the bearings in constant thrust. The action of the explosion in driving apart the pistons A and B draws together, by means of the oblique rods, the pistons C and D, compressing the charge between them, so that the negative work of compression is performed, not through the crank and connecting-rods, but directly through the oblique rods, and only the net useful work is transmitted to the crankshaft. The reciprocating parts are cushioned at each end of every stroke and the balance is perfect, practically all vibration being eliminated.

In the course of a report upon tests of a demonstration engine, the results of a thirty hours trial are summarized as follows:

	Corresponding mean pressure at 249 R. P. M. Pounds per sq. in.
Average B. H. P. during thirty hours.....	510
Power used to drive the fan.....	50
Power indicated in gas-pump.....	14
Friction of engine and gas-pump.....	67
Total (indicated H. P.).....	641
	63.4

The average consumption of gas per brake horse-power hour was 18.1 cubic feet, and the average lower calorific value of the gas was 470 B. T. U. per cubic foot, the volume, both for the engine and the calorimeter, being measured at the temperature and pressure of the room. This corresponds to a thermal efficiency reckoned on the brake power of just under 30 per cent. This efficiency, he says, is quite satisfactory, being nearly, if not quite, equal to that obtainable under similar conditions from any four-cycle gas-engine now on the market, and probably better than that of any two-cycle engine. On account of the rather large amount of power absorbed in the air-pump in these experiments, the ratio of brake horse-power to total indicated horse-power is rather low, being not more than 80 per cent, and the efficiency reckoned on the indicated power is correspondingly high (37.6 per cent). This is due to the high piston speed, and the cylindrical form of combustion chamber, which, together with the comparatively low mean pressure, led him to expect a higher indicated efficiency than has usually been obtained in gas engines hitherto. With the better pumping arrangements proposed in the new design, which would give higher mechanical efficiency, the engine when using coal gas, or any gas with a high calorific value as in the trials now reported on, will, he adds, be exceptionally economical in fuel.

## NOTES AND CORRESPONDENCE

### NOTE ON THE DETERMINATION OF CINEOL

In a previous article<sup>1</sup> I described a method for the determination of cineol in the essential oils of eucalyptus and cajuput, based on the relative stability of the former to permanganate solution. Since then some rather adverse criticisms of the method have appeared,<sup>2</sup> which, in the interest of those who may have in-

clination to try the process, perhaps call for some explanation.

In the first place, I feel that I can reasonably disclaim responsibility for the erratic results reported by these experimenters, because they appear to have adopted procedures of their own, using small quantities of oil and neglecting the precaution which I had recommended, namely, the checking of the purity of the cineol obtained in the assay process by the observation of its physical properties.

<sup>1</sup> THIS JOURNAL, 4, 592

<sup>2</sup> *Perf. and Ess. Oil Record*, 3, 295; 4, 348; Schimmel and Co., *Berichte*, April, 1913.

To take 5 cc. of oil in a "cassia" flask, oxidize with whatever permanganate the flask will hold, and report, without more ado, the volume of unoxidized oil as cineol, is not what I have advised, nor is it sufficient to ensure useful or reliable results. The examination of the cineol isolated is indispensable, not only for the purpose of detecting any unoxidizable substances, as camphor or paraffins, but also as a check on the completeness of the oxidation; for it not infrequently happens that an apparently satisfactory oxidation is yet incomplete, owing to some unnoticed irregularities in conditions or manipulation. But it is always possible to ascertain this, in the manner suggested, and unless this is done the results are inevitably uncertain and devoid of meaning.

Umney<sup>1</sup> states: "We have shown quite recently that this process is of little value for eucalyptus oils." This alleged demonstration has, however escaped me, unless he refers to Bennett's experiments, in which case, I admit, the conclusion would appear to be well founded. But if, in a well conducted oxidation, 70 per cent of reasonably pure cineol has been isolated, I consider it safe to assume that the oil in question contains really at least that amount, for, in the present state of our knowledge, the formation of cineol by oxidation of any other constituent of the oil, must be regarded as improbable. Hence, I maintain that the method, properly executed, cannot give results higher than the truth.

It is possible, of course, in a hasty assay, that a 70 per cent oil may yield 80 per cent or even 90 per cent of unoxidized product, but examination of the latter will immediately show its impurity, and incidentally the necessity of more careful repetition of the operation. But such results, due to faulty manipulation, should not be held up to the prejudice of the method, any more than in the case of a titration, where one has used an insufficient amount of the reagent.

As regards a second criticism,<sup>2</sup> that with oils low in cineol a loss occurs by oxidation of the cineol itself, especially in the presence of terpineol, I am quite ready to admit the possibility thereof, as the oxidation of cineol by excess of strong permanganate is a well known reaction. But what interests us here is the relative stability of cineol, and I have endeavored to show, and still hold, that it is possible so to conduct the reaction, that practically all of the oil except the cineol is oxidized with little, if any, loss of the latter.

For oils containing less than 50 per cent cineol, however, the method is not to be recommended, as the large amount of reagent and time required make it tedious and impracticable. The increasing alkalinity of the solution also tends to cause a loss of cineol.

But as such oils are in general inadmissible for pharmaceutical use, the difficulty is not serious.

Modifications of the method have been tried, in the hope of simplifying the procedure, or shortening the time, but no decided improvement has resulted. An acid permanganate solution reacts very quickly, but the results are less uniform. The mixture of permanganate and magnesic sulfate (used to ensure neutrality) is so slow in its action as to be impracticable. We have found, however, that it is not necessary to keep the assay very cold, except in the first stages of the oxidation. As the reaction diminishes in vigor, the operation may be conducted at the ordinary temperature without apparent loss of accuracy.

As regards the other methods suggested for the determination of cineol, the phosphoric acid and resorcinol processes are, in my experience, of little use in the presence of camphor or terpineol, and it is exactly these compounds which it is most important to detect.

FRANCIS D. DODGE

LABORATORY OF THE DODGE AND OLCOTT CO.  
BAYONNE, N. J., July 13, 1914

<sup>1</sup> *Loc. cit.*

<sup>2</sup> Schimmel and Co., *Loc. cit.*

## THE PRESENT STATUS OF THE GLASS BOTTLE INDUSTRY IN THE UNITED STATES

The glass bottle and hollowware industries of the United States have undergone important changes during the last bottle "season," and both the automatic and semi-automatic bottle machines have been improved and more widely adopted since the last report on these industries.<sup>1</sup>

When one considers that the manufacture of glass bottles by the use of machinery has been practiced only twenty years, the status of the mechanical blower is indeed remarkable. It was in 1882 that Phillip Arbogast was granted a patent wherein the method of prepressing a blank in a mold and then transferring it to another mold to be blown into finished form was claimed. This basic patent was sold to D. C. Ripley, a flint glass manufacturer of Pittsburgh, Pa., and the process was first put into operation in the early nineties in the manufacture of small wide-mouth ware. It was employed in the production of fruit jars in 1896 and about five years later was first used in the manufacture of narrow-mouth bottles.

Automatic machines came into use in 1904. At the present time 172 machines of this type are installed, an increase over last year of 21; a list of these installations follows:

LOCATION AND NUMBER OF AUTOMATIC MACHINES INSTALLED	
American Bottle Co., Newark, Ohio.....	28
This company manufactures beer, malt and water bottles. 210 gross of pint beer bottles and 165 gross of quart beer bottles are produced in 24 hours.	
American Bottle Co., Streator, Ill.....	24
17 six-arm machines are installed. Each machine produces 140 gross of quart beer bottles and 170 gross of pint beer bottles in 24 hours. 7 ten-arm machines, each of which will make 150 gross of quarts or 230 gross of pints in 24 hours, make up the remainder of the equipment.	
Ball Brothers, Muncie, Ind.....	11
This firm manufactures fruit jars.	
Charles Boldt Glass Co., Cincinnati, Ohio.....	14
All kinds of liquor ware.	
Dominion Glass Co., Montreal, Canada.....	4
General line.	
Dominion Glass Co., Hamilton, Ontario.....	4
General line.	
Dominion Glass Co., Wallaceburg, Ontario.....	3
Beer bottles and flasks.	
Dominion Glass Co., Redcliffe, Alberta.....	1
Beer bottles.	
Hazel-Atlas Company, Washington, Pa.....	11
General line.	
Hazel-Atlas Company, Clarksburg, W. Va.....	3
General line.	
Heinz Company, Sharpsburg, Pa.....	3
Condiment wares.	
Illinois Glass Co., Alton, Ill.....	22
Liquor, prescription and packers' wares. Total number of machines to be installed, 24	
Illinois Glass Co., Gas City, Ind.....	5
General line of prescription and liquor ware.	
Northwestern Company, Toledo, Ohio.....	2
Catsup and brandy bottles.	
Owens Automatic Bottle Co., Toledo, Ohio.....	1
Experimental plant.	
Owens Bottle Co., Fairmont, W. Va.....	12
Liquor, catsup and grape-juke bottles. The 12 machines installed are all of the ten-arm type. The output is as follows: 4-ounce grape-juke bottles, 360 gross in 24 hours; 9-ounce catsup bottles, 220 gross in 24 hours; 16-ounce grape-juke bottles, 195-200 gross in 24 hours.	
Owens Eastern Bottle Co., Clarksville, W. Va.....	5
Oval, round, square and flat prescription bottles, panels and other small ware.	
Thatcher-Baldwin Company, Elmira, N. Y.....	4
Milk jars.	
Thatcher-Baldwin Company, Streator, Ill.....	4
Milk jars. Each of the machines installed turns out about 100 gross of quart or 130 gross of pint milk bottles in 24 hours.	
Thatcher-Baldwin Company, Kane, Pa.....	4
Milk jars. Each machine produces 75 gross of quarts, 90 gross of pints, or 100 gross of 1/2 pints in 24 hours.	
Whitney Glass Co., Glassboro, N. J.....	7
Medicine bottles.	

The small ware output of the Owens machine is as follows: 1/2-ounce round prescriptions, 60 per minute; 1-ounce round prescriptions, 52 per minute; 2-ounce round prescriptions, 48 per minute; 4-ounce round prescriptions, 40 per minute; 8-ounce round prescriptions, 36 per minute; 16-ounce round prescriptions, 28 per minute; and 32-ounce round prescriptions, 18 per minute.

<sup>1</sup> See Hamor, *THIS JOURNAL*, 5, 951. On the glasses from which bottles are made, see Hamor, *Am. Druggist*, 63, 29; *THIS JOURNAL*, 6, 509.



minute. These data apply to practically all round, oval, French square, oblong and flat bottles. Panels from 4 ounces up are made at the rate of 38 per minute.

During the season 1913-'14 there was not only an increase in the number of automatic machines in operation, but an improvement in their mechanical equipment. The six-arm machine was changed to one of ten and, in some instances, to fifteen arms, thus increasing greatly the number of bottles produced. However, so far the Owens interests do not have a monopoly of the bottle industry, for the hand-operated machines and the semi-automatic contrivances still offer competition. But the time is rapidly approaching when the automatic machine will replace all other types as well as the hand blower; during the past year, several hand-blown ware manufacturers stated that unless some further concession was made in wages, they would install machines for producing narrow-mouth bottles, practically the only line now manufactured by hand.

The season was also productive of a number of improvements in increasing the efficiency of the semi-automatic machines. Manufacturers are of the opinion that the work of one man only, the gatherer, is necessary in operating semi-automatic machines, and most of the improvements were directed towards reducing the number of men employed. The three-shift system is becoming more generally adopted, for it has been shown that continuous production procured in this way is a great factor in helping to keep pace with the production of the automatic machines.

#### STANDARD BOTTLE CAPACITY

Ever since the introduction of automatic machines, the operators of hand-blown ware factories and officers of the Glass Bottle Blowers' Association have been much exercised by state legislation requiring exactness in the capacity of containers of all descriptions. By the old hand method it has always been impossible to produce bottles of exactly uniform capacity, this being evidenced by a provision in the wage scale which allowed variations below and above a given capacity. With the machine every bottle is of exactly the same capacity. Accordingly, while the disposition of state and municipal authorities to require exactness in bottle capacities has been strenuously opposed by the hand blowers, machine operators have been rather inclined to lend support to the formulation and enforcement of these statutes and ordinances.

A convention of the sealers of the United States was held in Washington during May of this year, at which ones in attendance urged that no enactments discriminatory to the interests of the hand blowers be adopted. New specifications in accordance with the laws now in force in certain of the states were presented by officials of the Glass Bottle Blowers' Association, and it is reported that they are regarded as reasonable in the matter of tolerance by certain of the authorities.

#### FOREIGN COMPETITION

Germany, France and Austria-Hungary were the leading exporters of bottles to the United States during the fiscal year ending June 30th. The values of the imports of bottles follow:

SOURCE	Value of bottles empty or filled	Value of bottles cut or ornamented
Germany.....	\$204,883	\$332,809
Austria-Hungary.....	143,086	299,978
France.....	277,439	115,232
United Kingdom.....	77,485	107,416
Belgium.....	439	141,436

W. A. HAMOR

NEW KENSINGTON, PA.  
September 1, 1914

#### THE HYDROCARBONS OF UTAH—A CORRECTION

Our attention has been called to certain inaccuracies in the above paper.<sup>1</sup> According to Messrs. Richardson and Forrest,<sup>2</sup>

<sup>1</sup> THIS JOURNAL, 5 (1913), 973

<sup>2</sup> Private communication.

"It is stated that Trinidad asphalt, supplied by the New York Testing Laboratory, contains 60.36 per cent of bitumen. This is at least 4 per cent out of the way. It is stated that it contains 3.94 per cent of organic matter insoluble in CS<sub>2</sub>. In view of my (Richardson) investigations on 'The Proximate Composition and Physical Structure of Trinidad Asphalt' published in Vol. 6 of the Proceedings of the American Society for Testing Materials, 1906, page 509, this is, of course, quite incorrect. It is, in reality, water of hydration in the clay which is lost on ignition on the determination of the mineral matter. The authors say that Bermudez and Trinidad have a tarry odor, than which nothing could be more absurd. The percentage of bitumen in the specimen of Bermudez furnished the authors by the N. Y. Testing Laboratory is stated as 90.93. It must have been considerably higher than that. The ultimate composition of the samples of the various bitumens, as given, are entirely wrong. The authors have evidently attempted to make a combustion on the material in its ordinary form, and not on the pure extracted bitumen. The percentage of sulfur, determined by the Eschka method is, of course, too low. They do not seem to be aware that the nitrogen in bitumens cannot be determined by a modified Kjeldahl method."

It seems that we were mistaken in the kind of materials furnished under the names Refined Trinidad Lake Asphalt, Refined Bermudez Lake Asphalt, and Gilsonite, for we believed that they were "pure" and not merely "purified commercial products which, however, were not free from all extraneous substances \* \* \* \*"

Samples of the hydrocarbons under discussion were re-analyzed by one of us (T. B. B.) and by the New York Testing Laboratory with the following results:

N. Y. T. L.	Trinidad R. A.	Bermudez R. A.	Tabbyite
Bitumen soluble in CS <sub>2</sub> .....	56.9%	92.5%	94.7%
Mineral matter.....	35.6	5.1	4.8
Fixed carbon.....	12.0	12.9	9.2
T. B. B.			
Bitumen soluble in CS <sub>2</sub> .....	57.5	92.3	....
Mineral matter.....	35.7	5.3	....
Fixed carbon.....	....	....	....
N. Y. T. L.	Gilsonite	Wurzelite No. 1	Wurzelite No. 2
Bitumen soluble in CS <sub>2</sub> .....	....	....	....
Mineral matter.....	....	....	....
Fixed carbon.....	13.6%	7.8%	7.5%

Our errors in Bitumen soluble in CS<sub>2</sub> were due to our not igniting the filtrates in order to determine the insoluble matter that passed through the asbestos filtering medium. What we reported originally as Fixed Carbon were in reality the non-volatile residues, minus ash, left from the fractional distillations, as shown in our Table IV.<sup>1</sup> Through an oversight an explanation of this was omitted. When determined according to the standard method for the proximate analysis of coal<sup>2</sup> very much lower results are obtained, as indicated above.

The "Organic Matter insol. in CS<sub>2</sub>" we obtained by difference. We were not acquainted with the article by Mr. Richardson, in which he points out the importance of the water of hydration in the clay. All ultimate analyses reported were made on the original materials furnished us, and *not* on purified samples specially prepared for the purpose. The modified Eschka method is used extensively in the west for sulfur, arsenic, molybdenum, vanadium and other determinations, and has been found to be very accurate, even with relatively volatile substances like certain coals and vegetable matter. Concordant analyses were obtained in all determinations reported. The last statement applies also to the nitrogen results.

<sup>1</sup> Loc. cit., 976.

<sup>2</sup> Jour. Amer. Chem. Soc., 21 (1899), 1116.

We wish to thank Messrs. Richardson and Forrest for their interest and friendly cooperation in this investigation, and for their criticism of the data published.

CARLOS BARDWELL  
B. ARTHUR BERRYMAN  
THOMAS B. BRIGHTON  
KENNETH D. KUHR

UNIVERSITY OF UTAH  
SALT LAKE CITY  
February 4, 1914

### REMEDIES FOR POTASH SHORTAGE

*Editor of the Journal of Industrial and Engineering Chemistry:*

A good deal of ridiculous although perhaps well-meant material is appearing in the daily and weekly press in regard to remedies for the potash shortage. Some of these are so far from the truth that it seems desirable to make some statement about the matter which is based on fact.

Various suggestions have been made in regard to the steps to be taken by farmers in reference to the shortage of potash in their fertilizers, caused by the greatly reduced shipments of potash from Germany since the first of August. Most of the fertilizer companies have endeavored to make the potash on hand go as far as possible by selling for the present brands of complete fertilizers containing only 2 or 3 per cent of potash and withholding from sale, brands containing larger amounts.

The suggestion that some or all of the potash be replaced by phosphoric acid is absurd, for every school boy knows that one plant food cannot take the place of another. There are some indirect fertilizers, such as lime, gypsum and salt that can release a limited amount of potash from some soils that contain hydrated silicates of alumina and potash. But if these soils have already been treated with lime or have received repeated dressings of the usual forms of fertilizer containing soluble phosphate with its accompanying gypsum, then the potash in the hydrated silicates has to a large extent already been replaced and the use of more lime or gypsum or salt could not be expected to release much additional potash. Ground limestone or oyster shells act too slowly to be used as potash releasers.

The residue of soda left in the soil by nitrate of soda is more effective in releasing potash than is gypsum and hence goods, in which the nitrogen is largely in the form of nitrate of soda, may have a special value in the present emergency.

It is often stated that decaying organic matter releases potash from the soil but there seems to be no direct evidence of this. On the contrary, Dr. S. Peacock states in the *American Fertilizer* of Sept. 5, 1914: "Several thoroughly competent researches have shown that decaying organic matter has little effect on converting inert mineral plant food in the soil into available form."

In any soil the amount of potash capable of being released by these indirect means is a very small fraction of the total potash in the soil, most of which exists in a form about as soluble as window glass. There is no known profitable method for rendering this inert potash of the soil available fast enough to provide for profitable crops. Whatever temporary expedients we may employ in the present emergency, we must keep in mind that the potash thus removed from the semi-available soil reserves must later be replaced if we are to maintain the soil's productiveness.

There is danger in the statement that farmers have been using an excess of potash. Crops use on the average about two and one-half times as much potash as phosphoric acid, while the average fertilizer sold contains only half as much potash as phosphoric acid; yet no one claims that we are using too much phosphoric acid. The potash remaining from previous fertilization is practically nothing except in the limited areas where a ton or more of fertilizer has been used per acre on truck crops.

Very rarely is half as much potash applied to the wheat, oats, corn or cotton crop as the crop removes.

The potash mines are so numerous and the stocks on hand so large that supplies can be promptly sent forward, as soon as European conditions permit freight shipments to be resumed.

H. A. HUSTON

NEW YORK CITY  
September 16, 1914

### DR. LEO H. BAEKELAND IN JAPAN

The letter printed below has been received by Dr. Jokichi Takamine from Prof. Dr. Joji Sakurai, Dean of the College of Science of the Tokio Imperial University, regarding the visit of Dr. Leo Baekeland to Japan:

"MY DEAR DR. TAKAMINE:

"I have duly received your favor of July 8th, introducing Dr. Baekeland, and also your letter of July 9th, regarding his visit to Japan.

"I had already been advised by your friend Mr. Shiohara concerning Dr. Baekeland's visit, and as I wanted to do my best to give him a rousing welcome, I notified the several members of both the Tokio Chemical Society and Society of Chemical Industry, and held a meeting on July 9th to discuss the plans for welcoming our distinguished visitor. Dr. T. Takamatsu, President of the Society of Chemical Industry, myself and three others were appointed as a reception committee.

"We completed arrangements on August 1st, and sent out over three hundred invitations for a dinner to welcome Dr. Baekeland on August 10th, under the joint auspices of over thirty of the leading members of the Tokio Chemical Society and the Society of Chemical Industry, as well as over twenty leading business men who are connected with chemical industry.

"The dinner was held at the Seiyoken Restaurant at Uyenopark, and despite extreme heat there were over sixty people present. It was one of the most successful dinners we have had recently. Dr. Baekeland seemed well pleased with the reception he received. By my colleagues' recommendation I served as the toast-master for the evening; my toast, of course, was in English, but as the majority of the people present were not conversant with English, it was printed in Japanese beforehand and was distributed among those present. Dr. Baekeland spoke for about half an hour on 'Original Research Work,' and Dr. K. Kondo interpreted his speech into Japanese. The event was a most pleasant and interesting one.

"We had expected that Dr. Baekeland's sojourn in Japan would extend to the middle of September, and it was my intention to ask him to deliver a general lecture before the gathering of students after their return to school from holidays, but we had to abandon this plan on account of Dr. Baekeland's limited stay in our country.

Very sincerely yours,

JOJI SAKURAI."

TOKIO, JAPAN, August 12, 1914

Professor Sakurai's toast to Dr. Baekeland was as follows:  
"YOUR EXCELLENCIES AND GENTLEMEN:

"I esteem it a great privilege to have been asked to preside over this dinner, and I have now the great pleasure to propose the toast of our distinguished guest—Dr. Baekeland. I am fully aware of the difficulty of the task I have to perform, however pleasant it may be, and I really think it unfortunate that some one more able and eloquent than myself has not been chosen for this important task. But, unworthy as I am of the chair, I can assure you all that I am second to none in the desire of extending a most hearty welcome to Dr. Baekeland. It is, moreover, a relief to me to think that our guest is a man of science, who cares more for plain words and naked facts than flowery speeches and diplomatic etiquette, a circumstance

which, when speaking in a foreign language, as I am now attempting to do, renders the task of the chairman somewhat easy.

"Now, I am sure you will all agree with me when I say that, although it is always a pleasure to us to welcome our American friends to this country and to have their company, this pleasure is enhanced on the present occasion by the fact that our guest and friend is an eminent chemist, who has greatly contributed to the progress of chemical industry by his important researches, among others, those on photographic papers, the electrolytic preparation of caustic soda and last, but by no means least, important—the manufacture of a new plastic, which has been named after him and which, as an insulating material and in various other ways, is finding more and more extended application. The importance of these researches has been widely recognized in America, for, among other honors, he has been awarded both the Nichols Medal and the Gibbs Medal from the American Chemical Society, the John Scott Medal from the Franklin Institute, and the Chandler Goff Medal from Columbia University, besides being elected at various times either the President or the Vice-President of the American Chemical Society, the American Electrochemical Society, the American Institute of Chemical Engineers, the Society of Chemical Industry, and several other important societies. We may further remember that as the President of the Section of Plastics of the VIIIth International Congress of Applied Chemistry Dr. Baekeland contributed, in no small degree, to the success of that important congress.

"The fact that, in spite of the almost unbearable heat of these days, when most people have deserted the town for cooler places in the country, some sixty chemists and men of business who are interested in chemical industry have assembled here this evening to greet the distinguished visitor will, I believe, show how greatly his work is also appreciated in this country and what admiration there is for his personality. Sixty is not a large number, but, as Dr. Baekeland will himself easily recognize, the warmth of their feeling in extending a hearty welcome to him is none the less very great, greater even than the heat of these days.

"It is true that Dr. Baekeland has, no doubt, inadvertently chosen the worst season in coming to this country, but from our self-interested point of view it is at a very opportune time, for the idea of establishing an independent chemical research laboratory, first suggested and propagated with enthusiasm by our mutual friend, Dr. Takamine, is now attracting a considerable amount of public attention, and an expression of opinion on any subject bearing either directly or indirectly on this movement by one of such wide experience and great attainment as Dr. Baekeland will, I am sure, be of very great value to us at this moment. With his permission, therefore, I would like very much to ask Dr. Baekeland to speak on any phase of this subject, and I am sure that I voice the sentiment of all present.

"In conclusion, I would express the hope that Dr. Baekeland may fully enjoy his visit to this country, that when he gets back to America he may carry with him a very pleasant remembrance of his visit, and that, keeping this pleasant remembrance, he may come back to us many times, not forgetting, however, to bring Mrs. Baekeland with him next time.

"And now, gentlemen, I give you the toast of our distinguished visitor—Dr. Baekeland."

#### AMERICAN ELECTROCHEMICAL SOCIETY TWENTY-SIXTH GENERAL MEETING NIAGARA FALLS, OCTOBER 1-3, 1914

The twenty-sixth general meeting of the American Electrochemical Society was held at Niagara Falls, October 1-3, 1914, with headquarters at the Clifton Hotel, Niagara Falls, Ontario.

#### PROGRAM OF PAPERS

The Physical Nature of Color (illustrated lecture), C. E. KENNETH MEES (Director Research Laboratory, Eastman Kodak Company).

1. The Evaporator and the Power Problem in Electrochemical Plants. OTTO MANTUIS.

2. On Electrometric Titrations. HENRY ZIEGEL.

3. The Sources of Impurities in Cathode Copper. LAWRENCE ADDICKS.

4. The Constancy of Base-Metal Thermocouples as Affected by their Micro-structure. O. L. KOWALKE.

5. The Reproducibility of the Copper Electrode. FREDERICK H. GETMAN.

6. The Electrolytic Determination of Nickel. N. JUDSON MARSH.

7. Electrodeposition of Lead from Lead Acetate Solutions. F. C. MATHERS.

8. Electrodeposition of Lead from Lead Lactate and Lead Formate Solutions. F. C. MATHERS AND B. W. COCKRUM.

9. Tin Salts of Mineral Acids. F. C. MATHERS AND B. W. COCKRUM.

10. On the Formation of a Badly-conducting Film on a Copper Anode in Copper Cyanide Solution. W. LASH MILLER.

11. Experiments on the Quantitative Determination of Radium. HERMAN SCHLUNDT.

12. Silicidized Carbon-Silfrax. F. J. TONE.

13. The Electrolytic Insulation of Aluminum Wire. C. E. SKINNER AND L. W. CHUBB.

14. Electro-Percussive Welding. C. E. SKINNER AND L. W. CHUBB.

Symposium—The Practical Side of Electrochemical Investigation, at the Fitzgerald Laboratories, Niagara Falls, N. Y. This symposium consisted of a number of informal demonstrations of apparatus, methods, and materials used in electrochemical investigations, or as electrochemical aids to chemical investigations.

#### EXCURSIONS

Foster's Flats. Arrangements were made for the excursion to be accompanied by a local authority on the flora, fauna and history of the locality.

Plants. Among those visited were the Power Houses on the American side, the Acheson Graphite Co. (who showed some features not hitherto exhibited), the Niagara Alkali Co., Spirella Corset Co.

The privileges of Niagara Falls Country Club were extended to members throughout the meeting. The Smoker on Thursday and the Dinner on Friday were held at the Clifton Hotel.

#### AMERICAN GAS INSTITUTE—NINTH ANNUAL MEETING OCTOBER 21-23, 1914 PROGRAM OF PAPERS

President's Address.

Refractory Materials for Coal and Water Gas Works. HERMAN RUSSELL.

Oil Tar Separation, Recovery and Disposal. R. E. WYANT.

Coal Gas Residuals. F. H. WAGNER.

Symposium—Operating Experiences under a Calorific Standard.

Efficiency Relation Existing between Various Test Burners, both Argand and Open Flame. F. H. GILPIN.

The Welding of High Pressure Mains. J. D. SHATTUCK.

The Installation and Maintenance of Services. R. B. DUNCAN.

The Installation, Repairing and Testing of Meters by a Small Company. CHARLES OTTEN, JR.

The Improvement of Distribution Employees. C. E. REINICKER.



The Year's Progress in Carbonization Methods. E. L. SPENCER.

Carbonization in Bulk. C. J. RAMSEUR.

The Operation of Inclined Retorts. FRANK HUBER.

Gas Chemists' Hand Book. W. H. FULWEILER.

An Electrical Process for Detarring Gas. F. W. STEERE.

A Method for the Determination of Hydrogen Sulfide in Gas.

A. B. WAY.

The Proper Specifications for, and Inspection of, Interior Gas Piping. A. E. TURNER.

Piping of Large Buildings for Gas. O. H. FOGG.

Utilization of Gas Appliances. W. J. SERRILL.

Estimating Accruing Depreciation and Features in Connection therewith as Related to matters of Accountancy. A. C. HUMPHREYS.

Accounting for Depreciation. HALFORD ERICKSON.

Methods and Facilities for Specifying and Testing Blowers, also Measuring Air and Steam Supply to the Water Gas Generators. J. M. SPITZGLASS.

Measurement of Gas in Large Volumes. J. F. WING.

Purifiers. C. E. PAIGE.

Care and Maintenance of Gas Holders. J. H. BRAINE.

Ammonia Purification. V. VON STARZENSKI.

The Fusibility of Ash in Coals Used in Gas Making. PERRY BARKER.

The Mode of the Decomposition of Coal by Heat. H. C. PORTER.

Gas Manufacture from the Point of View of Physical Chemistry. W. F. RITTMAN.

Illumination by Gas: Its Present Status and Its Future. C. O. BOND.

The Physical Installation of Gas Arcs. C. A. LUTHER.

Compensation of Meter Readers. H. C. SCHAFER.

Printing and the Care of Printed Stock. W. P. BAYLIE.

An Extension of the Dewey Decimal Classification System to Gas Engineering. D. S. KNAUSS.

Rate Making. WILLIAM MCCLELLAN.

## ANNUAL MEETING OF THE AMERICAN CHEMICAL SOCIETY CALLED OFF

At the meeting of the Directors of the American Chemical Society in New York on September 21, 1914, it was decided to hold no annual meeting of the Society this fall.

## SOME ECONOMIC ASPECTS OF INDUSTRIAL CHEMISTRY—A CORRECTION

In the article published under the above title, THIS JOURNAL, 6, 678, the paragraph beginning at the bottom of column 1, page 681, and the first sentence in the next paragraph should read as follows:

"From 1877 down to the close of 1912 there were taken out in Germany 8,062 German patents, or 224 per year, dealing with the utilization of coal-tar hydrocarbons and their by-products; it has been estimated that not more than one out of every hundred has secured financial returns for its owners. During the years 1895 to 1903, 382 German patents, or at the rate of 48 per year, were taken out in the inorganic chemical industries.

"It would be an interesting subject for speculation to consider the intellectual effort involved in the 8,062 coal-tar patents as compared with the intellectual effort required for the 382 inorganic patents."

BERNHARD C. HESSE

90 WILLIAM ST., NEW YORK  
September 8, 1914

## PERSONAL NOTES

Congress has provided \$200,000 for a Chemistry Building at the Bureau of Standards. Plans are now in preparation, but it will probably be two or three years before the building is completed.

Dr. Jokichi Takamine of New York City will present his paper on "The Chemical Industry of Japan" before the Detroit Section of the A. C. S. either on October 30th or November 27th.

Prof. R. H. Fernald of the University of Pennsylvania was recently appointed consulting engineer of the U. S. Bureau of Mines.

The Chicago Section of the A. C. S., at its regular meeting on September 11th, discussed the following subject: "How can we raise the moral and financial standing of our profession?"

Mr. William A. Williams, Chief Geologist General Petroleum Co., San Francisco, Cal., has been appointed chief of the new oil department of the U. S. Bureau of Mines, with headquarters at Washington, D. C.

Harry A. Curtis, assistant professor of chemistry at the University of Colorado, has returned after a year's leave of absence, during which time he took graduate work in chemistry at the University of Wisconsin, receiving the degree of doctor of philosophy.

The Executive Committee of the Chicago Section of the A. C. S. have instituted a bureau composed of chemists of recognized standing, which invites inquiry from any who desire advice as to the best method of procedure to overcome the handicap resulting from the scarcity of foreign-produced chemicals and products, and to answer inquiries and to supply, when possible, information such as cannot be obtained through

the usual channels, or to direct inquiries to reliable sources of information.

Irene Hunt Davis, instructor in chemistry at the University of Washington, has been promoted to be assistant professor of chemistry.

Several citizens of Toronto have agreed to contribute \$15,000 for five years to enable the University of Toronto to increase its research work.

The Pittsburgh Section of the A. C. S. held its 109th regular meeting at the University of Pittsburgh on September 17th. The program was as follows: "A Correlation between Certain Physical Properties and the Chemical Composition of Glasses, D. E. Ward Tiltson. "Crystalline Glazes—A Thermal and Optical Study of the System  $\text{Na}_2\text{O} \cdot \text{ZnO} \cdot \text{SiO}_2$ " (illustrated by Specimens and Lantern Slides), A. A. Klein.

The Detroit Section of the A. C. S. holds its meeting on the last Friday of each month at the Employers' Association rooms on the seventh floor of the Stevens Building.

The 109th meeting of the American Institute of Mining Engineers will be held at Pittsburgh, Pa., October 8 to 10, 1914. This meeting is to be under the auspices of the Committees on Iron and Steel, Petroleum and Gas, Coal and Coke, and Non-Metallic Minerals.

The meeting of the Southern California Section of the A. C. S. on September 19, 1914 took the form of a Picnic Excursion Venice, to which members, their families and friends were invited. All lunched together on the beach at 1 P.M. The afternoon was spent in games, races, bathing, lounging and all the usual and unusual Venice pleasures. The committee had arranged for a Special Fish and Chicken Dinner at 6 P.M.

at the Chafing Dish Inn, on the ocean front, near the picnic grounds.

Mr. John Lothrop Gray, formerly assistant general superintendent of the Tide-Water Oil Co., Bayonne, N. J., is now identified with the Pierce Oil Corporation, St. Louis, Mo., as manager of the refining and producing departments.

Dr. Friend E. Clark has resigned his position as professor of chemistry in Center College, Danville, Kentucky, to become professor of chemistry in West Virginia University.

Phlander Raymond Gray, one of the first refiners of oil in

this country, died at his home in Aberdeen Road, Elizabeth, N. J., on September 14, 1914. At the time of his retirement three years ago, he was manager of the refineries of the Standard Oil and Tide-Water Oil Companies, near Elizabeth.

Dr. Frederick G. Cottrell has been appointed Chief Chemist of the U. S. Bureau of Mines.

Dr. L. H. Baekeland reached New York City on September 22nd, returning *via* San Francisco from Yokohama, Japan, where he found it necessary to give up his tour around the world on account of the war in Europe.

## GOVERNMENT PUBLICATIONS

By R. S. McBRIDE, Bureau of Standards, Washington

**NOTICE**—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate. Consular Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington. The regular subscription rate for these Consular Reports mailed daily is \$2.50 per year, payable in advance, to the Superintendent of Documents.

### DEPARTMENT OF AGRICULTURE

**Rules and Regulations for Carrying out Provisions of Insecticide Act of 1910.** Circular 34, amendment 3. 2 pp. This amendment is to the rules regarding collection and examination of specimens of insecticides, Paris greens, lead arsenates, and fungicides.

**Acidity as a Factor in Determining the Degree of Soundness of Corn.** H. J. BESLEY and G. H. BASTON. Department Bulletin 102. 45 pp. Paper, 10 cents. This professional paper from the Bureau of Plant Industry shows how the acid test may be used in the commercial grading of corn. "It is intended for chemists, grain buyers, and all interested in grading corn, more especially in the corn belt and at terminal markets."

**Classification and Grading of Cotton.** D. E. EARLE and W. S. DEAN. Farmers Bulletin 591. 23 pp. Paper, 5 cents. This is a contribution from the Bureau of Plant Industry, intended to give in a popular manner the names, classification, and description of the different grades of cotton.

**Potash Salts and Other Salines in the Great Basin Region.** G. J. YOUNG. Department Bulletin 61. 96 pp. Paper, 15 cents. This contribution from the Bureau of Soils "embodies the results of investigations carried on in cooperation with the United States Geological Survey and the McKay School of Mines, Reno, Nevada with a view to determining the existence or non-existence of sources of potash salts in the basin region."

**Bacteriological and Chemical Study of Commercial Eggs in the Producing Districts of the Central West.** Under the direction of M. E. PENNINGTON, Associated with M. K. JENKINS, E. Q. ST. JOHN and W. B. HICKS. Department Bulletin 51. 77 pp. Paper, 40 cents. This contribution from the Bureau of Chemistry "gives details of an extensive study of the commercial eggs and makes recommendations for improvement in handling. While the study was made in the central west, the bulletin is equally of interest to all sections where eggs are produced in commercial quantities and are sent to egg-breaking or other packing establishments." The plates which illustrate this paper are also published on one sheet entitled "Egg Candler Chart."

**Ability of Streptococci to Survive Pasteurization.** S. HENRY AYERS and WILLIAM T. JOHNSON, JR. Separate from Journal of Agricultural Research, 2, 321-30. A contribution from the Bureau of Animal Industry.

**Bacteria Concerned in Production of Characteristic Flavors of Cheese of Cheddar Type.** ALICE C. EVANS, E. C. HASTINGS and E. B. HART. Separate from the Journal of Agricultural Research, 2, 167-92. A contribution from the Bureau of Animal Industry prepared in cooperation with the Wisconsin Agricultural Experiment Station.

**Relation of Action of Certain Bacteria to Ripening of Cheese of Cheddar Type.** E. B. HART, E. G. HASTINGS, E. M. FLINT and ALICE C. EVANS. Separate from the Journal of Agricultural Research, 2, 193-216. See previous article.

**Regulations Governing Meat Inspection.** Bureau of Animal Industry Order No. 211. Paper, 10 cents. This confidential publication was released on July 30th for general distribution. Its provisions take effect November 1st of this year.

### CENSUS BUREAU

**Census Statistics by States.** The statistics of population, agriculture, manufactures, mining, etc., for each of the states, as collected for the 1910 census, have been reprinted in pamphlets. These may be secured upon application by those interested; in general, no charge is made for these.

### BUREAU OF FOREIGN AND DOMESTIC COMMERCE

**South American Markets for Drug Products, Patent and Proprietary Medicines, Surgical Instruments, and Dental Supplies.** E. A. THAYER. Special Agents Series No. 85. 75 pp. Paper, 10 cents. This report is a very timely one as it gives in considerable detail, for many drugs and other products of chemical interest, the quantity and value of the imports from the United States for recent periods. The statistics are given for each of the South American countries separately, so that those seeking South American markets can tell as to the particular portion of the country where their products might find sale. (See also information under Consular Reports given below.)

### BUREAU OF STANDARDS

**Units of Weights and Measures.** Circular 47. 68 pp. This circular supersedes the earlier publication entitled "Tables of Equivalents of the United States Customary and Metric Weights and Measures." It includes numerous definitions of the fundamental units and their relation to sub and multiple units for length, area, volume, capacity and mass. There is included a brief discussion of standards for measurements; and the proper spelling and abbreviations for the various units are given. Tables of equivalents from 1 to 999 units are given for converting the customary (English) units to metric units and *vice versa*.

**Standard Methods of Gas Testing.** Circular 48. 180 pp. Paper, 35 cents. This circular contains suggestions as to location and equipment of gas testing laboratories, a description of some of the accepted forms of apparatus, directions for the making of the various tests, and recommendations as to the interpretation of experimental results. It does not discuss the testing work necessary for good works control; it deals rather with methods which are intended for use in city or state official





"butter" from the seeds, of the malma or illupei tree in India is described. (P. 908.)

The mineral products of Ireland include coal, iron ore, fire clay, bauxite, rock salt, barytes, soap stone, ocher, umber, and pyrite. (P. 909.)

The construction of large blast furnaces in Rouen, France, was started, to use ore from Spain, Algeria, and Sweden. [Report of consul dated July 22.] (P. 938.)

The use of *esparto* fiber from Algeria, for the manufacture of paper, mats, etc., is described. (P. 972.)

High pressure incandescent gas lamps are being tried at Montevideo, Uruguay, using gas at a pressure of 2 to 2.5 meters of water. The mantles are inclosed in silica globes. (P. 990.)

The Egyptian phosphate output is increasing, being shipped principally to Japan. (P. 991.)

Peach kernels from California have been shipped to Germany to be used in the manufacture of prussic acid, and "bitter almonds." (P. 1110.)

The market for American cottonseed oil in India is discussed. (Pp. 1111-5.)

The possibility of Americans obtaining a supply of German dyestuffs via Holland is discussed. (P. 1118.)

Rubber shipments from the Amazon valley show a slight decrease. (P. 1119.)

The principal mineral products of Alsace-Lorraine are iron ore, coal, salt, potash, petroleum, and asphalt. (Pp. 1126-7.)

The cultivation of kapols for fiber, in Ceylon is described. (P. 1160.)

The status of the iron, zinc, lead, copper, coal, petroleum and sulfur industries in Japan is discussed. (Pp. 897-907.)

Information as to rubber cultivation in India is given. (P. 1034.)

An appropriation of \$50,000 for promoting trade with Latin America is now available. (P. 1041.) A list of publications on South American trade is given. (Pp. 1012-20.)

Many requests have just been received from "Latin American countries" for various articles, including: Soap, cement, paper, starch, sugar, matches, oils, paints, drugs, photographic supplies, glassware, enameled ware, kerosene, coal, coke, soda, pig iron, galvanized iron, sheep dip, wax candles, malt, copper, and tin plate. (Pp. 849, 929, 977, 1109, 1042, 1156.)

An immediate market is needed for many supplies from Latin America, including: Cacao, wax, hides, tallow, balata, quebracho wood and extract, divi-divi, bones, sodium nitrate, copper, tagua nuts, sarsaparilla, tin, tungsten, rubber, copper, silver, and linseed. (Pp. 1010, 1071, 1156.)

A demand is received from Canada for shipments of steel, window glass, white lead, and flaxseed. (P. 1011.)

## BOOK REVIEWS

**The Occupational Diseases, their Causation, Symptoms, Treatment and Prevention.** By W. GILMAN THOMPSON, M.D. New York and London: D. Appleton and Company. 1914. Pp. xxvi + 724, with 118 illustrations. Price, \$5.00 net.

The reviewer recently referred to the growing interest which various American organizations are taking in the diseases of occupation.<sup>1</sup> Until the publication of this treatise, however, there had been no work of reference on the subject by an American authority on industrial hygiene. "To supply in some measure this lack, the present work has been undertaken, particularly with the aim of meeting the needs of American practitioners of medicine, as well as those whose industrial or philanthropic interests require a comprehensive summary of the nature and prevalence of the occupational disease hazards as they obtain in this country."

In preparing this work, which is more comprehensive than Arlidge's "Diseases of Occupation," Weyl's "Arbeiterkrankheiten," Roth's "Kompendium der Gewerbekrankheiten," Hirt's "Krankheiten des Arbeiter," Albrecht's "Gewerbehygiene," Layet's "Gewerbepathologie," or Oliver's "Diseases of Occupation," Dr. Thompson has enriched medical science with much new material. His investigations of the phenomena of industrial diseases, some of which are published herein for the first time, and still more his improvement of professional treatment have won for him a permanent reputation; but above all else he is inclined to assist his fellow-men to the utmost of his power. And this he has done in this noteworthy treatise, the preparation of which, as even one familiar with but medical propaedeutics can observe, has been a labor of love.

The work is divided into seven parts: Part I, History Classification, General Pathology and Etiology; Part II, General Remedial Measures; Part III, Diseases Due to Irritant Substances; Part IV, Diseases Due to Harmful Environment; Part V, Special Occupational Diseases; Part VI, Influence of Special Conditions on the Occupational Diseases; and Part VII, Miscellaneous Occupational Diseases Grouped by Industries not Included in the Foregoing Classification. There are also four appendices: Tabulated List of the Principal Harmful Substances and Their Effects; Tabular List of Important In-

dustries in which the Workman is Subjected to Several Hazards; Tabulated List of the Principal Industries in which Dust Constitutes the Essential Hazard; and Main Provisions of Existing Laws (1914) Relative to the Reporting of Occupational Diseases by Physicians. Theoretical toxicological details are omitted as are discussions of disputed scientific points.

Owing to the general excellence of all parts of this treatise, one were unappreciative of diligence did he not feel tempted to refrain from critical comment thereon. However, an endeavor to be helpful prompts the reviewer to indicate whereby its usefulness might be further augmented.

Dr. Thompson is, of course, eminently equipped with the very special knowledge required to describe and discuss the pathology of the lesions set up and the preventive measures necessary to combat them; but his descriptions of manufacturing operations, evidently taken largely from medical reports, and his purely chemical considerations, are less accurate; in fact, the book is in need of chemical revision.

Shellac is not "secreted by a scale-forming insect" (p. 166); lead does not enter into the manufacture of aluminum foil (p. 199); it should have been noted that acrolein vapors arise when metal articles are dipped into molten fat in galvanizing and tinning (p. 305); the account of the formation of nitrous gases (p. 372) is inaccurate; the highly poisonous nature of osmium tetroxide (p. 375) is due to the reduction by the tissues to metallic osmium; picric acid (p. 375) is manufactured by the nitration of phenol; "chinin" and "chinon" are mentioned (pp. 376 and 688), the first as a "petroleum by-product," reference being had to quinine and quinone; paraphenylenediamine (p. 381) is not manufactured from petroleum; asphalt is classed under "insoluble inorganic dusts" on p. 400, and under "organic dusts" on p. 692; plate glass is cast, not blown (p. 409), although the time is approaching when it will be blown mechanically; oxalic acid is not properly classified on p. 420 (in this connection it may be noted that at the only oxalic acid manufactory in this country the preparation is carried on in open vessels); sodium and potassium chlorides are not "made by electrolysis" (p. 589); flint is hardly a "silicious variety of quartz" (p. 620); and cinnabar is mentioned in the place of stibnite on p. 665.

<sup>1</sup> THIS JOURNAL, 6, 526.

The chemical industry offers naturally a wide field for the occurrence of occupational diseases; but it can take credit for the way in which the incidence of industrial poisoning has been minimized in view of the extent of the risks which often threaten. Despite all hygienic regulations, however, the risk of poisoning cannot be entirely banished: wholly to prevent accidents and illness is as impossible as totally to prevent accidents by the mechanical guarding of machinery.

Dr. Thompson's book is not burdened with morbidity and mortality statistics, eight pages being devoted to these subjects. This is pleasing, for undigested statistics are indeed a fruitful source of nightmare. Apparently alarming increases in disease, based on comparison with ten, twenty or fifty years ago, generally overlook the most probable cause for the increase, the more complete and accurate statistics of the present day. In this connection, it may be noted, however, that later statistics relating to the German chemical industries than those for 1907 (p. 29) were available prior to the publication of this work; for instance, the disease statistics of the chemical industries for 1911 were reported by Curschmann in *Chemische Industrie*, 36, 58, and the annual report of the Königlich Preuss. Regierungs- und Gewerbeberichte for 1912 appeared in the *Chemiker-Zeitung*, 37, 1020.

Regarding the strictly medical phases of the subject, the following critical comments are made in the hope that they may be suggestive when the book is revised:

The intraocular action of certain new alloys which have industrial application, e. g., those of iron with aluminum, nickel, tungsten, chromium and copper, is not mentioned; we are aware that Graham-Rogers regarded "brass-founders' ague" as "zinc poisoning," but it is more likely due to the inhalation of zinc oxide and not zinc fumes (p. 170); until recently only founders were exposed to the fumes of molten zinc or brass, but the perfection of the acetylene-oxygen torch has greatly extended autogenous welding and brazing, and from this "braziers' disease," identical with "brass-founders' ague," has arisen; concerning copper (p. 188), Lehmann has shown experimentally that as an industrial poison this metal is not important; in connection with the manufacture of electric accumulators (p. 224), the Regulation of the Secretary of State of Great Britain, dated 1903, should have been mentioned; when lead is temporarily fixed in the tissues, this is later mobilized and it is likely that it enters the circulation as a soluble lead-protein compound, which might have been mentioned on p. 247 in connection with the occurrence of the lead in the urine in plumbism; Bezzola<sup>1</sup> has shown that the serious nature of the poisoning is indicated during the period of lead colic by the cytological evidence, although albumin may be absent or present (p. 248); no mention of the "electrolytic bath" treatment for the removal of lead is made on p. 283; no space is devoted to very rare nickel carbonyl poisoning on p. 298, but the very thorough investigations of Armit<sup>2</sup> were worthy of mention; in regard to Shuber's report (p. 299), it may be observed that argyrosis occurred in the silvering of glass pearls owing to the introduction of a silver nitrate solution into the beads by mouth-suction—suction pumps are now employed; concerning vanadium poisoning (p. 300), Lees<sup>3</sup> failed to find that there is any such disease as "vanadiumism" arising from external contact with vanadium compounds; regarding amyl acetate (p. 307), 5 mg. per liter produce irritation of the mucous membranes; cyclohexanol acetate is also of technical importance and 3 mg. per liter produce irritation; the hygienically preferable use of benzine and sulfur chloride for vulcanizing is not mentioned on p. 319; it is not noted that carbon monoxide (p. 323) is not widely distributed in the blood poisoned by it, as shown by Wachholz<sup>4</sup>; diethyl sulfate is not included (p.

330); carbon tetrachloride, chloroform, and the chlorinated derivatives of acetylene are not referred to; dinitrochlorobenzene, which causes a violent dermatitis,<sup>1</sup> should have been mentioned on p. 344; concerning roborite (p. 344), in the Witten roborite factory during 1890-7 almost all the workmen had been ill; regarding the prognosis of phosphorus poisoning (p. 354), mention is not made that early operative interference has succeeded in preserving the periosteum which enabled the new bone to form; regarding Oliver's views (p. 364), it has been demonstrated that drying paints emit no metallic vapors, although they do produce carbon monoxide;<sup>2</sup> it should have been mentioned on p. 381 that paraphenylenediamine leads to poisoning generally from the use of ursoil as a dye, and that its irritant action on the mucous membranes of the respiratory tract is more prominent than its production of kidney inflammation; it is not noted on p. 400 that asphalt dust may cause severe affection of the cornea in workmen exposed thereto, and the full discussions of the lesions produced by the dust and vapor of asphalt in a number of contributions by Truc and Fleig are not referred to; besides wearing a respirator, goggles, a regulation sand blasting helmet, and heavy canvas overalls, leggings and gloves, sand blast operators (p. 418) should be provided with a heavy leather belt, equipped with a snaphook to engage a ring in a collar near the hose nozzle, to hold the hose securely and to prevent its getting out of the grasp; ones acquainted with the glass industry in this country state that buccal musculature atrophy and pneumatocoele are practically unknown among blowers (cf. p. 409); regarding the effect of siliceous dusts, Rossel<sup>3</sup> has recently concluded that laborers in the glass, porcelain, lime and cement industries are relatively favored with regard to tuberculosis; the author differs from Rambousek (p. 443), who considers that "industrial poisoning from tobacco is not proved," the unpleasant fumes given off during the boiling of linseed oil with oxidizing agents (see p. 462) may also be prevented by closely fitting covers and condensation of the fumes; the action of ultraviolet rays should have been referred to on p. 512; concerning the effects of radium (p. 514), a good discussion of possible injuries is given in *Deut. med. Wochschr.*, 40, 633, wherein it is shown that handling radioactive substances may cause disturbances of general health, particularly of the blood picture and of the function of the genital glands, besides lesions of the skin; welders should wear aluminum helmets, equipped with combination blue and red glass lens for the eyes (p. 515); it should have been mentioned on p. 570 that Butler<sup>4</sup> has shown that chronic carbon monoxide poisoning is one of the principal etiological factors in nystagmus occurring among coal miners; the disease aspects of dermatitis developed when aniline dyes with turpentine or varnish act on the skin<sup>5</sup> might have been noted on p. 579; on p. 586 no reference is made to phenylenediamine, which is widely used in the dyeing of hair or furs and frequently causes eczematous, cutaneous eruptions, which irritant effects are due to an oxidation product, quinone-dimine, and may be prevented by using a sufficient amount of a salt with a reducing action along with the oxidizing agents required for dyeing; Rybak's elaborate investigations on so-called poisoning by fire-damp are not referred to on p. 612; in regard to ceramic glazing (p. 619), tile-dipping machines are now in use by which handling of the glaze is reduced to a minimum, and the fettling and cleaning of the glaze from the edge of the tile is practically abolished; Eickmeyer's study of the injuries to the cornea by artificial fertilizers<sup>6</sup> was worthy of note on p. 633; and on p. 657 the use of alkaline solutions in skinning fruit is not referred to.

W. A. HAMOR

<sup>1</sup> Bernstein, *Lancet*, 172, 1534.

<sup>2</sup> *This Journal*, 6, 91 and *Drugs, Oils and Paints*, 30, 10.

<sup>3</sup> *Münch. med. Wochschr.*, 61, 756.

<sup>4</sup> *Ophthalmoscope*, 1912, 680.

<sup>5</sup> See Sachs, *Arch. Dermatol.*, 116, 555.

<sup>6</sup> *Inaug. Diss.*, Rostock, 1911.

<sup>1</sup> *Soc. med. biol.*, session June 28, 1913.

<sup>2</sup> *J. Hyg.*, 1907, 526; 1908, 565.

<sup>3</sup> *Eng. Min. J.*, 92, 99.

<sup>4</sup> *Vierteljahrschr. Ger. Med.*, 47, 205.

**The Electrical Conductivity and Ionization Constants of Organic Compounds.** A bibliography of the periodical literature from 1889 to 1910 inclusive, including all important work before 1889 and corrected to the beginning of 1913. Giving numerical data for the ionization constants at all temperatures at which they have been measured; and some numerical data of the electrical conductivity. By HEYWARD SCUDDER, B.A., B.S., M.D. Pp. 568. New York: D. Van Nostrand Company. 1914. Price, \$3.00.

The data which are given in this book cover the period of time stated in the sub-title. Since 1910, the ground has been covered by the *Tables Annuelles Internationales des Constantes et Données Numériques*.

The amount of labor expended by Dr. Scudder in the compilation must have been enormous. It is to be hoped that the end attained will justify this and that the book will be used extensively. Twenty-three pages of "Explanation" at the beginning show the arrangement of the material and give a detailed description of the tables. The tables follow, and then are given Formula Index, Author List, Subject Index, and Journal List.

Without having undertaken a careful and detailed study of the tables, it appears to the reviewer that the work as a whole has been well done. The appearance of the book, including the printing and general arrangement, is excellent. The data will save many chemists much searching through the literature. This book will find its place more and more, as time goes on, covering as it does a certain field of physical organic chemistry of the past. It should find a place as a reference book in every chemical library.

K. G. FALK

**Chemistry of Dyeing.** By JOHN KERFOOT WOOD, D.Sc. New York: D. Van Nostrand Company. 1913. 7½ X 5. Pp. 80 + viii. Price, 75c. net.

This book is a small monograph giving the present status of the various theories relating to the dyeing process. Without undertaking an extended discussion of the various theories involved, the author has nevertheless given their main points in a very concise manner. He has also criticized the different theories which have been put forward to account for the phenomena of dyeing in an intelligent and conservative manner. The subject is approached from the standpoint of the chemist rather than the technical dyer, and while this book would be of considerable interest to the general chemist and those chemists who are interested in dyestuffs and dyeing processes, it is doubtful if the manner of presentation of the facts would be of any special interest to the practical dyer. The nature of the dyeing process is discussed as a question in physical chemistry, and of course this is the only proper method of approaching the subject in a scientific manner. The author is unencumbered with preconceived notions and is unprejudiced by any one particular view or theory. Consequently he has given a very fair criticism of the different theories and in a rather impartial manner has suggested a means of bringing the several theories together under one statement of fact. In order to do this he has had to take a divided view of the dyeing process and instead of regarding it as simple in character and as the result of a single operation, he adopts the view that there are two stages in the dyeing process, the first of which may be called the absorption stage where the dyestuff or coloring matter is simply absorbed from solution, and the second a fixation stage where the coloring matter so absorbed becomes fixed permanently in the fiber which is dyed. In the absorption stage it is probable that the dyestuff is merely absorbed by the fiber by a process of diffusion of the dye solution into the fiber substance and there is no particular theory needed to account for this, it being entirely governed by the usual laws of absorption and diffusion. Owing to the peculiar structure of the textile fibers this absorption and

diffusion of the dyestuff solution is slow and is not uniformly distributed throughout the fiber but allows of a greater deposit of the dyestuff at the surface so that the process can be included under absorption phenomena. As the fibers are considered to be hygroscopic colloids, the manner in which they absorb dyestuffs is in accordance with general laws; for instance, all colloidal substances absorb others according to the law embodied in the expression  $C_1 C_2^v = k$ , where  $C_1$  and  $C_2$  represent concentration in the aqueous and in the other phase, respectively at the end of the absorption,  $k$  is a constant and  $v$  is a constant coefficient. Zacharias has shown that this formula may be deduced mathematically from the laws of diffusion and is applicable not only to the dyeing of textile fibers but also to other substances such as charcoal, aluminum hydroxide, etc. The formula is the same as that representing the distribution of a substance between immiscible solvents where homogeneous solutions are formed. The second phase of the dyeing process may bring into play other forces besides those of a purely physical character. There may be more or less of a chemical reaction involved in the union between certain dyestuffs and fibers or between certain dyestuffs and mordants previously fixed in the fibers. There may be also various physical forces operating in this same connection and a theory of fixation which might be suitable to explain the action of one dyestuff toward silk for instance, might not satisfactorily explain the action of some other dyestuff towards cotton. Therefore, it cannot be hoped to explain all the processes of the dyeing of all manner of dyestuffs on the various textile fibers by one simple theory. The author gives at the end of the book a very complete bibliography referring to the original papers by various chemists on the subject of the chemistry of dyeing. There is one omission to be noticed in the book and that is the work of Prof. Bancroft on the theory of the dyeing process, but probably this omission has been due to the fact that the matter for the book was written previous to the appearance of Prof. Bancroft's published work.

J. M. MATTHEWS

**The Organometallic Compounds of Zinc and Magnesium.** By HENRY WREN, M.A., D.Sc., Ph.D. Chemical Monographs, No. 1, Edited by A. C. CUMMINGS, D.Sc., F.R.S.E. New York: D. Van Nostrand Company. 1913. Pp. viii + 100. Price, 75c. net.

The latest series of chemical monographs on special subjects of which this volume is the first is intended primarily for advanced students. The organometallic compounds of magnesium which comprise the greater part of the book, include the group of reactions discovered by Barbier and developed in so many directions by Grignard. All of the important syntheses are given, together with copious references. The first section (12 pp.) contains the introduction and the experimental method and precautions to be observed in carrying out the reactions; the second section (60 pp.) describes the various syntheses with the Grignard reagents; the third section (8 pp.) summarizes some of the theoretical views of the constitution of the reagents and the mechanism of the reactions; while in the fourth section (13 pp.) the analogous reactions and syntheses with the zinc organometallic compounds are given. A bibliography and index complete the book.

The material contained in this monograph will be most useful for the purpose for which it is intended. The general appearance and arrangement is excellent and the size of the volume is very convenient. It can be recommended most heartily to those who desire a concise and fairly complete description of the reactions and reagents in question.

K. G. FALK

**Chemistry and its Borderland.** By ALFRED W. STEWART. 8vo. Longmans Green & Co. 1914. Price, \$1.25.

This book, written for the entertainment and instruction



of the uninformed reader, serves its intended purpose rather more happily than does the typical work of this character. The first three chapters, more or less perfunctory and haphazard, are not a felicitous introduction to the body of the work; but after this rather unsatisfactory beginning, the book takes on a decidedly better tone. The essays which follow are entertaining expositions, written in great part from an historical point of view, and in narrative form on the following topics: immuno-chemistry; colloids and the ultramicroscope; the work of the spectroscope; chemistry in space; the inert gases; radium; niton; transmutation; the nature of the elements; chemical problems of the present and future. Considering the fact that the author presupposes no chemical knowledge on the part of the reader, these chapters are skillfully written; for, though fragmental, they are consecutive and clear, while the points most emphasized in each discussion are those which are important as well as entertaining.

The book is not wholly free from incautious and extravagant statements and conjectures, into which nearly all writers of popular scientific expositions seem nowadays to be betrayed. A statement such as that "in the earlier days of chemistry the atom of an element was supposed to be the most minute form of matter which could exist" (p. 223) conveys a false impression, especially when it follows one to the effect that "the discovery of radioactive phenomena has undermined the whole structure of the physics and chemistry of yesterday," so that "at the present time we are hurriedly endeavoring to dismantle the older edifice, while utilizing as much of its material as is suitable in the construction of a more modern erection" (p. 214). Such a statement is not only exaggerated, but is essentially false. One might have hoped, also, not again to have encountered in a book which will be read by many as authoritative, the definite and unqualified conjecture that the energy of radioactive disintegration may one day supplant that of our present coal supply (p. 233) nor the anticipation that the synthesis of polypeptides even remotely points to the subsequent creation of living protoplasm (p. 246). However, such remarks are rare in this book and seldom mar the quality of a generally wholesome and very entertaining group of essays.

The chemist reader will be interested in the chapter on transmutation, in which the author supports with lively argument the contention that the recent experiments of Collie, Patterson and Ramsay demonstrate the synthetic transmutation of the elements.

The last two chapters are an effective appeal to the public at large for the more intelligent support of scientific investigation. Though the need for such appeal is, happily, not as urgent here in America as it probably is in England, correct information nevertheless, concerning the supreme practical value of pure scientific research and the best practical means for its encouragement, cannot be too widely disseminated.

F. BARRY

**The Silicates in Chemistry and Commerce.** By W. ASCH AND D. ASCH. A. B. SEARLE, Translator. New York: D. Van Nostrand Co. 456 pp. Price, \$6.00.

The present volume under its promising title represents the elaboration of a thesis having for its object the consideration of a general theory of the structure of silicates analogous to the systems of organic chemistry.

The first two sections give an excellent historical review of existing theories concerning the structure of silicates and their critical examination. In the following sections their new theory is advanced, according to which two types of Si and Al radicals are supposed to exist. The one type supposes the union of six molecules of  $\text{Si}(\text{OH})_4$ , and similarly of six molecules of  $\text{Al}(\text{OH})_3$ , which unite to form closed rings, maintaining the tetra- and tri-

valencies of Si and Al. These complexes are called hexites. Similarly, by the combination of five molecules of  $\text{Si}(\text{OH})_4$ , and five of  $\text{Al}(\text{OH})_3$ , respectively, the closed ring radicals to be known as pentites are formed.

These radicals provide the nuclei for the acids and anhydrides. "The Al hydrohexites or hypodentites unite with those of silica and *vice versa*, the hydroxyl groups in the ortho position in these rings splitting off the elements of water, two other OH groups, also in the ortho position of the silicon ring, losing their hydrogen atoms and forming free  $\text{H}_2\text{O}$ ." Types consisting exclusively of hexites are termed primary, those containing both hexite and pentites are secondary. The analogs of the benzene ring are then carried out step by step down to base and ring isomerism. Thus, as an illustration of the latter case, orthoclase and microcline are cited. The theory is extended to molybdc and tungsten complexes.

In the discussion of the structure of clays the authors assume the formula  $6\text{H}_2\text{O} \cdot 6\text{Al}_2\text{O}_3 \cdot 12\text{SiO}_2$  for kaolins and maintain the existence of two kaolinic acids, *a* and *s*, according to whether they possess central Al or Central Si rings. The authors even predict the plasticity of these kaolinic acids, claiming that the *a* type is more plastic owing to the greater content of water of constitution. In applying the hexite-pentite theory of clays to various phenomena, the writers make many statements not in agreement with known facts. According to them, clays are not mixtures of "clay substance," feldspar and quartz, but are of unitary structure. The translator does not help matters by introducing supplementary notes utterly irrelevant to the question of the constitution of clays. Occasionally he saves the day by correcting such a statement as: "Vitriified clays must be more easily attacked by acids than unvitriified ones." The discussion is extended to ultramarines, Portland cement, slags, dental cements, glasses and glazes. The treatment of some of these subjects might be termed weird. We learn, for instance, that Portland cements are single hexite-pentite compounds and not mixtures and that the tri-calcium silicate is a purely hypothetical compound. Considerable attention is given to dental cements from the h. p. standpoint and even their physiological behavior is discussed. Definite formula are assumed for many glasses and glazes, a procedure surprising to ceramists whose experience tends to support the view of silicate mixtures. Other topics treated are those relating to water of crystallization; the dissociation theory; the constitution of simple acids; the h. p. theory and carbon compounds; the Archid hypothesis; the h. p. theory in stereochemistry with reference to di- and polymorphism and isomorphism; optical properties, etc. In a summary, reply is made to various critics of the German edition.

Any attempt to bring unity into the confusion of the views relating to silicate structure is to be welcomed. In so far as the statement of their hexite-pentite theory is concerned, the authors deserve a respectful hearing. They cannot be expected to produce complete proofs for their assumption, considering the enormous difficulties offered by laboratory research along these lines and the comprehensiveness of their fundamental statement. On the other hand, the proofs cited by them based on the work of others are open to serious doubt and the evident inaccuracy of many statements does not encourage confidence in the conclusions. The present writers would have fared much better had they tested their theory by the critical examination of a small number of typical silicates instead of endeavoring to explain in a wholesale manner every kind of fact relating to silicates.

For the reader who desires to secure sound technical information concerning silicates the book is of no value.

A. V. BLEININGER

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**Silicidized Carbon-Silifrax.** By F. J. TONE. *Preprint: American Electrochemical Society*, Vol. 26, 1914, No. 12, pp. 1-10.

**Surface Combustion.** By W. A. BONE. *American Gas Light Journal*, Vol. 101, 1914, Nos. 9, 10 and 11, pp. 129-132, 145-148 and 161-164.

**Tanning Chemistry in 1913.** By W. FAHRION. *Zeitschrift fuer angewandte Chemie*, Vol. 27/1, 1914, No. 60, pp. 457-464.

**Teaching Chemistry and Physics, Significance of Experimentation in.** By OTTO FRIEDRICH. *Dingler's Polytechnisches Journal*, Vol. 329, 1914, Nos. 33 and 34/5, pp. 513-516 and 533-536.

**Tin and Antimony, Metallurgy of.** By W. A. COWAN. *Preprint: American Institute of Metals*, 1914, No. 19, pp. 1-36.

## RECENT INVENTIONS

By C. L. PARKER, Solicitor of Chemical Patents, McGill Building, Washington, D. C.

**Welding Copper.** E. E. Reigle, June 2, 1914. U. S. Pat. 1,008,404. Copper is boiled for two hours in a solution of chlorate of potash and then welded.

**Rubber Composition.** J. W. Aylsworth, June 2, 1914. U. S. Pat. 1,008,609. The composition comprises rubber, a chlorine derivative of naphthalene, and sulfur.

**Treating Match-Splints.** W. G. Wey, June 2, 1914. U. S. Pat. 1,008,700. Flaming and non-glowing properties are imparted to match-splints by subjecting them to a solution of phosphorus in paraffin.

**Dehydrating Perborates.** O. Liebknecht, June 2, 1914. U. S. Pat. 1,008,740. Crystallized perborates are dehydrated by heating them to 50° to 70° C. in the presence of an alcohol.

**Purifying Hydrocarbons.** F. Richter, June 2, 1914. U. S. Pat. 1,008,763. Liquid hydrocarbons are purified by mixing them with finely divided active carbon and agitating the mixture in contact with oxygen containing gases.

**Isoprene.** F. Webel, June 2, 1914. U. S. Pat. 1,008,859. Isoprene is produced by treating a methyl-butenol ester at an elevated temperature and in a vaporized state with alumina.

**Rubber Compounds.** L. Collardon, June 2, 1914. U. S. Pat. 1,008,882. A cellulose xanthate solution is first produced. This is treated in order to expel free moisture and reduce the product to a plastic form. The plastic product is then mixed with sufficient rubber to produce a coherent mass. The product is then vulcanized.

**Aluminum Chlorid.** A. M. McAfee, June 2, 1914. U. S. Pat. 1,009,096. Aluminum chlorid is recovered from oily residues by first removing the oil from such residues, heating to a carbonizing temperature, and treating with chlorin.

**Manufacture of a Substance Resembling Natural Rubber.** Weissgerber and Keller, June 2, 1914. U. S. Pat. 1,009,107. A fraction of the first running of benzol taken up to 25° C., free from carbon disulfid, is subjected to the action of sodium in the presence of a small quantity of ammonia.

**Refractory Lining for Furnaces.** O. Serpek, June 2, 1914. U. S. Pat. 1,009,131. The refractory lining consists essentially of aluminum nitrid with a backing of carbon and aluminous material.

**Stable Crystalline Sodium Bisulfite.** H. Howard, June 9, 1914. U. S. Pat. 1,009,177. Sulfur-dioxid is passed through a

dioxid is absorbed in a second solution which is later added to the mother liquor from the recovered bisulfite. Additional sulfur-dioxid is then passed through the mixed solutions.

**Light-Colored Adhesive Substance from Sea-Weeds.** A. Krefling, June 9, 1914. U. S. Pat. 1,009,382. The dark colored skin of the stalks of sea-weed is first removed and the stalks are then leached with water and treated with chemicals to effect dissolution.

**Preparation of Hydrogen by Auto-Combustion.** G. F. Jaubert, June 9, 1914. U. S. Pat. 1,009,446. Hydrogen is formed by autocombustion of a metal, a metalloid, or an alloy which has been previously heated to a very high temperature, the combustion being effected in the presence of an oxidizing agent. The process is characterized by the fact that the oxidizing agent is exclusively formed by steam, all expensive reagents being avoided. The metals, metalloids, and alloys which it is stated give the best results are ferro-alloys, particularly those having as base silicon, aluminum, manganese, or calcium.

In the apparatus illustrated, *a* is a vat of refractory material, *f* is a steam pipe and *g* are nozzles for injecting the steam into the vat. A suitable quantity of metal, metalloid, or alloy, is introduced into the vat and to this metal, metalloid, or alloy, a suitable quantity of a cheap alkaline base such as lime may be added. The contents of the vat are then kindled by any well known method. Owing to the heat, the reaction of steam becomes superheated and is decomposed by its contact with the metal at a high temperature, the oxygen of the water being utilized for the combustion of the metal, metalloid, or alloy, and the hydrogen escaping through the pipe *h*. The slag may be extracted at *b* during the operation.

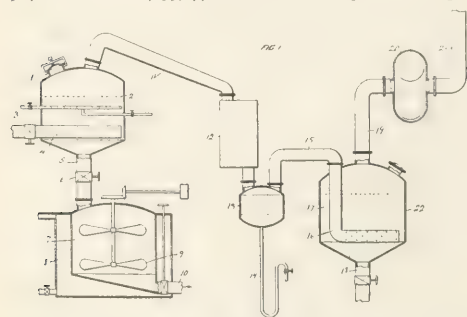
**Sulfite Liquor.** Moore and Wolf, June 9, 1914. U. S. Pat. 1,009,565. Calcium bisulfite having a predetermined proportion of free sulfurous acid is produced by refrigerating milk of lime to a constant predetermined temperature and passing sulfur dioxide through it.

**Treating Electro-Metallurgical Products.** F. J. Tone, June 9, 1914. U. S. Pat. 1,009,674. Impurities are removed from electro-metallurgical products used for abrasives or refractory purposes by treating with chlorin gas in sufficient quantities to combine with the impurities present.

**Smelting Ores.** F. J. Machalske, June 9, 1914. U. S. Pat. 1,009,709. A basic charge composed of iron ore, graphite, and a basic flux, is formed and subjected to the action of an electric current.

**Set-Adjusting Cement Waterproofing Compound.** C. Ellis, June 16, 1914. U. S. Pat. 1,009,974. The composition comprises stearate of lime containing an excess of lime in admixture with sodium aluminate, the proportion of stearic acid in combination with lime in the composition being approximately 25 per cent of the total lime content.

**Nitro Products from Petroleum and Tar.** A. S. Flexer, June 16, 1914. U. S. Pat. 1,009,976. Nitro products are produced from a mixture of petroleum and tar by subjecting petroleum in the presence of tar to the action of concentrated nitric acid.



solution containing a sulfite until a bisulfite separates from the solution. This bisulfite is recovered and the excess of sulfur-



**Colored-Cement Product.** H. A. Gardner, June 16, 1914. U. S. Pat. 1,100,129. A non-hydrous paste containing a pigment and an unsaponifiable protective vehicle is mixed with the cementitious material to be colored.

**Device for Indicating Naphthalene in Illuminating Gas.** E. S.-C. Deville, June 16, 1914. U. S. Pat. 1,100,231. The apparatus comprises essentially an obstruction or baffle arranged in the passage for the gas and partially obstructing this passage. This obstruction will increase in the course of the operation by the naphthalene of the gas that is deposited upon the restriction creating a partial obstruction there. A differential pressure gauge, the two branches of which open upon either side of the constriction, indicates at any moment the loss of charge resulting from the resistance thus created.

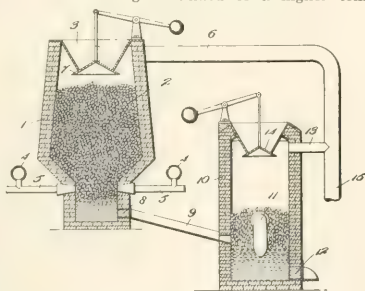
The current of gas is caused to traverse a narrow passage, in such a manner that it is easy to cool it or to heat it to temperature  $t$  indicated by a thermometer. The gas, however, retains its own temperature up to the precise point at which it enters the constriction raised to  $t^\circ$ . This peculiarity is essential. It is preferable and even important, in certain cases, to dry the gas prior to causing it to pass into the indicating apparatus.

To do so, the gas to be tested is dried by means of dry calcium chlorid, the test vessel with the pipe in which the gas whose percentage of naphthalene it is desired to ascertain is circulating, in such a manner that the desiccation is effected at the temperature of the gas in the pipe. No quantitative analysis should be attempted until three or four cubic meters of gas have passed over the chlorid of calcium at a velocity of from 40 to 50 liters per hour, in the case of a chlorid test vessel with a capacity of approximately a liter. Finally, in the intervals

of time comprised between the quantitative analysis of naphthalene, the gas should never cease to circulate in the chlorid test vessel at a velocity which can be reduced to 10 or 15 liters per hour. When the gas is very poor in naphthalene, far too much time may elapse before the naphthalene deposited upon the constriction of the apparatus produces a suitable obstruction. In this case, artificial priming or starting may be employed. The gas previously dried under the conditions set forth, passes for some minutes through a branch into a small test tube containing naphthalene in the form of powder, at the temperature of the laboratory. Thus enriched, this gas will very rapidly partially obstruct the restriction. The direct passage for the gas to the constriction of the indicating apparatus is then reestablished.

**Phosphoric Acid and its Derivatives.** F. S. Washburn, June 16, 1914. U. S. Pat. 1,100,639. A furnace is charged with a mixture of phosphate rock, silicious material, and a carbonaceous material and combustion of the carbonaceous material is effected by air blown into the furnace. This combustion liberates a portion of the phosphorus contained in the phosphate

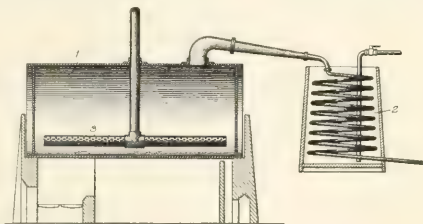
rock. The heated mass is then discharged into an electric furnace and the heating continued to a higher temperature



through the agency of electricity until substantially all of the phosphorus has been eliminated.

**Arsenate of Lead.** Dow and Barstow, June 16, 1914. No. 1,100,686. An alkali is added to a solution of a soluble acid arsenate and the resulting solution mixed with a solution of lead chlorid, so that arsenate of lead is precipitated.

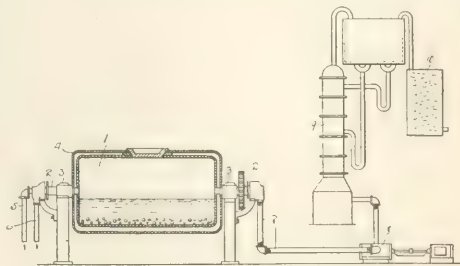
**Treating Oil.** J. A. Dubbs, June 23, 1914. U. S. Pat. 1,100,717. The process is designed to maintain the oil under treatment at a temperature at which a breaking up of the hydro-



carbon occurs. The hydrocarbons are heated to a point at which they would be broken up if mingled with air. Air is then forced through the oil and the heat is maintained by the chemical reaction produced.

**Alkyl-Esters of Morphin.** M. C. Traub, June 23, 1914. U. S. Pat. 1,100,998. Morphin is dissolved in a solution of alkyl phenyl ammonium hydroxid and the solution boiled for several hours.

**Chloroform.** Griswold and Strosacker, June 23, 1914. U. S. Pat. 1,101,025. Chloroform is produced by agitating carbon tetrachlorid, water, and iron, together, a portion of the



iron being in the form of relatively coarse particles. A quantity of hard balls are mixed with the particles of iron so that the latter are gradually reduced in fineness as the agitation continues.

# MARKET REPORT

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR THE MONTH OF SEPTEMBER, 1914

## ORGANIC CHEMICALS

Acetanilid.....	Lb.	30	@	32
Acetic Acid (28 per cent).....	C.	1.50	@	1.65
Acetone (drums).....	Lb.	11	@	12
Alcohol, denatured (180 proof).....	Gal.	33	@	35
Alcohol, grain (188 proof).....	Gal.	2.52	@	2.54
Alcohol, wood (95 per cent).....	Gal.	45	@	47
Amyl Acetone.....	Gal.	2.50	@	2.75
Aniline Oil.....	Lb.	@		
Benzoic Acid.....	Lb.	@		
Benzol (90 per cent).....	Gal.	-	@	-
Camphor (refined in bulk).....	Lb.	@		
Carbolic Acid (drums).....	Lb.	42 1/2	@	50
Carbon Bisulfide.....	Lb.	10	@	15
Carbon Tetrachloride (drums).....	Lb.	-	@	15
Chloroform.....	Lb.	30	@	35
Citric Acid (domestic), crystals.....	Lb.	90	@	1.00
Dextrine (corn).....	C.	1.07	@	3.32
Dextrine (imported potato).....	Lb.	@		
Ether U. S. P., 1900).....	Lb.	18	@	24
Formaldehyde.....	Lb.	8 1/2	@	9 1/2
Glycerine (dynamite).....	Lb.	24 1/2	@	25 1/2
Oxalic Acid.....	Lb.	20	@	22
Pyrogallol Acid (bulk).....	Lb.	2.50	@	-
Salicylic Acid.....	Lb.	1.25	@	-
Starch (cassava).....	Lb.	3 1/4	@	4
Starch (corn).....	C.	2.39	@	2.50
Starch (potato).....	Lb.	-	@	-
Starch (rice).....	Lb.	@		-
Starch (sago).....	Lb.	-	@	-
Starch (wheat).....	Lb.	5	@	10
Tannic Acid (commercial).....	Lb.	60	@	66
Tartaric Acid, crystals.....	Lb.	65	@	70

## INORGANIC CHEMICALS

Acetate of Lead (brown, broken).....	Lb.	7 1/4	@	7 1/2
Acetate of Lime (gray).....	C.	1.50	@	1.55
Alum (lump).....	C.	2.75	@	3.00
Aluminum Sulfate (high-grade).....	C.	1.50	@	2.00
Ammonium Carbonate, domestic.....	Lb.	10	@	11
Ammonium Chloride, gray.....	Lb.	6 1/2	@	7
Aqua Ammonia (drums) 16°.....	Lb.	2 1/4	@	2 1/2
Arsenic, white.....	Lb.	-	@	13
Barium Chloride.....	Lb.	-	@	-
Barium Nitrate.....	Lb.	-	@	-
Barytes (prime white, foreign).....	Ton	19.00	@	25.00
Bleaching Powder (35 per cent).....	C.	2.75	@	3.00
Blue Vitriol.....	C.	4.50	@	4.75
Borax, crystals (bags).....	Lb.	3 1/4	@	4 1/2
Boric Acid, crystals (powd.).....	Lb.	7 1/4	@	8
Brimstone (crude, domestic).....	Long Ton	22.00	@	22.50
Bromine, bulk.....	C.	40	@	50
Calcium Chloride, fused.....	C.	60	@	65
Chalk (light precipitated).....	Lb.	8	@	10
China Clay (imported).....	Ton	15.00	@	17.00
Feldspar.....	Ton	-	@	-
Fuller's Earth, powdered, Foreign.....	Ton	-	@	-
Green Vitriol (bulk).....	C.	55	@	60
Hydrochloric Acid (18°).....	C.	1.15	@	1.65
Iodine (resublimed).....	Lb.	3.75	@	4.00
Lead Nitrate.....	Lb.	8 1/2	@	9
Litharge (American).....	Lb.	5 1/2	@	5 3/4
Lithium Carbonate.....	Lb.	1.25	@	1.30
Magnesium Carbonate.....	Lb.	6	@	6 1/2
Magnesite "Calcined".....	Ton	55.00	@	-
Nitric Acid, 36°.....	Lb.	37 1/2	@	42 1/4
Phosphoric Acid (sp. gr. 1.75).....	Lb.	28	@	28 1/2
Phosphorus.....	Lb.	-	@	-
Plaster of Paris.....	Bbl.	1.50	@	1.70
Potassium Bichromate, 50°.....	Lb.	15	@	-
Potassium Bromide.....	Lb.	80	@	85
Potassium Carbonate (calcined), 80 @ 85°.....	C.	17	@	-
Potassium Chlorate, crystals.....	Lb.	-	@	-
Potassium Cyanide (bulk), 98-99%.....	Lb.	25	@	30
Potassium Hydroxide.....	C.	35.00	@	40.00
Potassium Iodide (bulk).....	Lb.	3.15	@	3.25
Potassium Nitrate (crude).....	Lb.	-	@	-
Potassium Permanganate (bulk).....	Lb.	55	@	65
Quicksilver, Flask (75 lbs.).....	Lb.	75.00	@	80.00
Red Lead (American).....	Lb.	5 3/4	@	6
Salt Cake (glass makers').....	C.	55	@	65

Silver Nitrate.....	Oz	34	@	37
Soapstone in bags.....	Ton	10	@	12.00
Soda Ash (48 per cent).....	C.	67 1/2	@	72 1/2
Sodium Acetate.....	Lb.	5	@	7
Sodium Bicarbonate (domestic).....	C.	1.00	@	1.10
Sodium Bicarbonate (English).....	Lb.	2 1/4	@	3
Sodium Bichromate.....	Lb.	4 1/2	@	5
Sodium Carbonate (dry).....	C.	60	@	80
Sodium Chloride.....	Lb.	8 1/4	@	8 1/2
Sodium Hydroxide, 60 per cent.....	C.	1.55	@	1.57 1/2
Sodium Hyposulfite.....	C.	1.60	@	1.90
Sodium Nitrate, 95 per cent, spot.....	C.	1.90	@	2.00
Sodium Silicate (liquid).....	C.	90	@	1.25
Strontium Nitrate.....	Lb.	-	@	-
Sulfur, Flowers (sublimed).....	C.	2.20	@	2.60
Sulfur, Roll.....	C.	1.85	@	2.15
Sulfuric Acid, 60° B.....	C.	85	@	1.00
Talc (American).....	Ton	15.00	@	20.00
Terra Alba (American), No. 1.....	C.	75	@	80
Tin Bichloride (50°).....	Lb.	13	@	14
Tin Oxide.....	Lb.	45	@	47
White Lead (American, dry).....	Lb.	5 1/2	@	5 1/2
Zinc Carbonate.....	Lb.	8 1/2	@	9
Zinc Chloride (granulated).....	Lb.	4 1/2	@	5
Zinc Oxide (American process).....	Lb.	5 1/2	@	6 1/2
Zinc Sulfate.....	C.	2.35	@	2.70

## OILS, WAXES, ETC.

Beeswax (pure white).....	Lb.	50	@	55
Black Mineral Oil, 29 gravity.....	Gal.	13 1/2	@	14
Castor Oil (No. 3).....	Lb.	8 1/2	@	9
Ceresin (yellow).....	Lb.	12	@	22
Corn Oil.....	C.	5.95	@	6.00
Cottonseed Oil (crude), f. o. b. mill.....	Gal.	35 1/2	@	36
Cottonseed Oil (p. s. y.).....	Lb.	57 1/2	@	6
Cylinder Oil (light, filtered).....	Gal.	21 1/2	@	32
Japan Wax.....	Lb.	20	@	24
Lard Oil (prime winter).....	Gal.	92	@	95
Linseed Oil (raw).....	Gal.	55	@	57
Menhaden Oil (crude).....	Gal.	35	@	-
Neatsfoot Oil (20°).....	Gal.	96	@	98
Paraffine (crude, 120 & 122 m. p.).....	Lb.	3 1/2	@	3 1/4
Paraffine Oil (high viscosity).....	Gal.	27	@	28
Rosin ("F" grade) (280 lbs.).....	Bbl.	4.05	@	4.10
Rosin Oil (first run).....	Gal.	25	@	-
Shellac, T. N.....	Lb.	17	@	18
Spermaceti (cake).....	Lb.	30	@	31
Sperm Oil (bleached winter), 38°.....	Gal.	70	@	71
Spindle Oil, No. 200.....	Gal.	18	@	19
Stearic Acid (double-pressed).....	Lb.	9	@	11
Tallow (acidless).....	Gal.	64	@	66
Tar Oil (distilled).....	Gal.	30	@	31
Turpentine (spirits of).....	Gal.	46	@	48

## METALS

Aluminum (No. 1 ingots).....	Lb.	19	@	20
Antimony (Hallet's).....	Lb.	11	@	12
Bismuth (New York).....	Lb.	2.10	@	2.15
Bronze powder.....	Lb.	-	@	-
Copper (electrolytic).....	C.	11.87 1/2	@	-
Copper (lake).....	C.	12.12 1/2	@	-
Lead, N. Y.....	C.	3.85	@	-
Nickel.....	Lb.	-	@	-
Platinum (refined).....	Oz.	50.00	@	52.00
Silver.....	Oz.	51 1/4	@	-
Tin.....	C.	31.75	@	32.00
Zinc.....	C.	5.37 1/2	@	6.00

## FERTILIZER MATERIALS

Ammonium Sulfate.....	C.	2.67 1/2	@	2.75
Blood, dried.....	Unit	3.20	@	-
Bone, 4 1/2 and 50, ground, raw.....	Ton	27.50	@	-
Calcium Cyanamid.....	Unit of Ammonia	2.22 1/4	@	2.40
Calcium Nitrate (Norwegian).....	C.	-	@	-
Castor meal.....	Unit	-	@	-
Fish Scrap, domestic, dried.....	Unit	3.40	@	-
Phosphate, acid, 16 per cent bulk.....	Ton	8.00	@	-
Phosphate rock; f. o. b. mine:				
Florida land pebble, 68 per cent.....	Ton	2.25	@	2.50
Tennessee, 70-80 per cent.....	Ton	5.00	@	5.50
Potassium, "muriate," basis 80 per cent.....	Ton	-	@	-
Pyrites, furnace size, imported.....	Unit	-	@	-
Tankage, high-grade.....	Unit	3.25	@	10

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## TABLE OF CONTENTS

EDITORIALS:			
Research: What—Who—Where—Why.....	880	A Large Incubator for Laboratory Use. By F. Alex McDermott.....	939
ORIGINAL PAPERS:		A Proposed New Standard Loop for Use in Bacteriological Tests of Disinfectants. By A. D. St. John.	940
The Biochemical Oxygen Demand of Sewages. By Arthur Lederer.....	882	Note on Substitute for the Blast Lamp. By Paul J. Fox.....	940
Notes on the Composition of Midcontinental Petroleum. By F. W. Bushong.....	888	A Convenient Form of Weighing Burette. By H. S. Bailey.....	941
Effect of Pressure on Yields of Products in the Destructive Distillation of Hardwood. By R. C. Palmer.....	890	SYMPOSIUM ON AMERICAN DYE INDUSTRY:	
Oils of the Coniferae: III. The Leaf and Twig and the Cone Oils of Western Yellow Pine and Sugar Pine. By A. W. Schorger.....	893	Introductory. By Chairman Allen Rogers.....	941
The Effect of Resene on the Lathering of Soap Solutions. By Chas. H. Herty and C. W. Willard.....	895	Dyestuffs and Textile Industry. By J. Merritt Matthews.....	942
Preliminary Note on Dyes and Other Products from the Waste Liquor of the Soda Cellulose Process. By Marshall P. Cram.....	896	Campaign for American Dyestuff Industry. By Arthur Prill.....	945
Some Rapid Methods for Glass Analysis. By E. C. Sullivan and W. C. Taylor.....	897	Coal Tar Colors of America. By I. F. Stone.....	946
The Composition of Milk as Shown by Analyses of Samples of Known Purity Made by the Massachusetts State Board of Health. By Hermann C. Lythgoe.....	899	Needs of the Textile Industry. By Alfred L. Lustig.	950
Some Characteristics of Chlorine-Bleached Flour. By C. A. A. Utt.....	908	The Position of the American Tar Distiller. By D. W. Jayne.....	952
Determination of Prussian Blue in Tea. By G. W. Knight.....	909	Relieving the Dyestuff Crisis. By Bernhard C. Hesse	953
An Investigation of the Diastase of Alfalfa and the Effect of Rapid Curing upon the Food Value of Alfalfa. By Ralph C. Shuey.....	910	CURRENT INDUSTRIAL NEWS:	
The Origin of Vanillin in Soils—Vanillin in Wheat and in the Water in which Wheat Seedlings Have Grown. By M. X. Sullivan.....	919	The President's Address before the Chemical Section of the British Association for the Advancement of Science; Patent Medicines in Great Britain; British Foreign Trade in August; Some Data of German and Austrian Foreign Trade; German Railroad Management; German Chemical Interests in Russia; The Match Industry in Russia; Temperature Conditions in Coke Ovens; The Disposal of Residuals in Gas and Coke Plants; United States Mineral Oil Exports; Testing Motor-Cars with Town Gas; Spelter; Mining in South Africa; Platinum Ore in Southern Nevada; Sanitation in Vera Cruz; Note..	953
An Exact and Easy Method for Preparing a Neutral Ammonium Citrate Solution. By J. M. McCandless.....	921	NOTES AND CORRESPONDENCE:	
The Influence of Fineness upon the Availability of Bone Meal. By S. S. Peck.....	922	Note on Antiseptics; Note on Water Purification by Ozone; Water Purification by Ozone—with Report of Ann Arbor Plant—Note; Preliminary Note on Iron in Florida Soils; Note on Colorimetric Method for Vanadium; Lubricant for Stopcocks, etc.; The American Institute of Mining Engineers; The National Council for Industrial Safety; American Leather Chemists' Association; The Chemical Societies in New York City.....	958
A Rapid Method for the Determination of Camphor and of Certain Essential Oils when in Solution in Alcohol. By W. B. D. Penman and W. W. Randall.....	926	PERSONAL NOTES.....	961
Study of the Methods for Extractions by Means of Immiscible Solvents from the Point of View of the Distribution Coefficients. II. By J. W. Marden and Vanna Elliott.....	928	GOVERNMENT PUBLICATIONS.....	963
LABORATORY AND PLANT:		BOOK REVIEWS: Chemistry in America; Chemical Reagents; Sammlung Vieweg, Heft 2. Anorganische Peroxyde und Persalze; Rapid Method for the Chemical Analysis of Special Steels, Steel-making Alloys, and Graphite.....	966
The Explosibility of Grain Dusts. By Harold H. Brown.....	934	NEW PUBLICATIONS.....	968
The Recovery of the Spent Lime from Causticizing Operations. By James H. Payne.....	937	RECENT INVENTIONS.....	969
		MARKET REPORT.....	970



## EDITORIALS

### RESEARCH

#### WHAT—WHO—WHERE—WHY

Industrial development, of the sort that comes with new and better processes, materials, and machinery together with improved methods of manipulation and production, independent of the influences of domestic and foreign trade relations, tariff or financial systems or legislation, must, as it always has, depend directly on the systematic searchings of the engineers, chemists and physicists familiar with present shortcomings and with the possibilities of their elimination. The urgent need of such development work has been repeatedly demonstrated by both chemists and engineers for many years, but, it must be confessed, with but little effect on those responsible for the appropriations without which it remains as impossible as if the need were not recognized nor the necessary talent available. The need is real and the talent is to be had, therefore, any lack of progress can be directly traced to lack of ability to convince financial managements that the employment of the talent is necessary or that it will be profitable.

Anything that will serve to help out this situation by demonstration or argument is worth while and worthy of encouragement on the broadest grounds. Such, for example, is the presidential address of Mr. A. D. Little, directed particularly toward the chemical industries and more especially toward the development of chemical products and processes rather than the engineering necessarily involved to make these industrial realities.

The extent of the influence of this address needs no better demonstration than the editorial notice given to it by the most excellent and conservative English journal, *Engineering* (quoted in full below).

Unfortunately some of the force of Mr. Little's arguments and the fundamental importance of the thing have been lost in subsequent quibbles over the meaning of the word "research," used by him as a name for the general and systematic finding of remedies for existing faults in the materials, processes, machinery or mechanical equipment of industrial plants. The trouble arises from the fact that the term has been for so long used in a narrow academic sense, entirely divorced from commercial utility, by men calling themselves scientific and regarding any search for knowledge as proper research only when the result has no money value. Is it any wonder, then, that a tempest in a teapot has arisen, first, on the part of the school-masters and their kind, who object to the desecration of their sacred "research" for the vulgar procedure of trade and money-making, and then on the part of financiers of the industries who fear that Mr. Little is urging them to spend money for that sort of research which its oldest advocates insist must not yield returns if true and proper.

#### REAL VS. ACADEMIC RESEARCH

"In a recent presidential address to the American Chemical Society, Mr. A. D. Little emphasized the importance of re-

search work in industrial operations, and if the term can be rightly interpreted few will care to dispute his contention. The term 'research' is, however, a much abused one, and by chemists, at any rate, is generally made to cover not only investigations of fundamental importance, such as those of Willard Gibbs into chemical and physical equilibrium, but also mere measurements by some third-year students of, say, the refractive indices of a series of compounds, work, which though possibly quite valuable, could be equally efficiently effected by a grocer's apprentice. In fact, measurements as fully entitled as these to be classed as research are made as a part of the daily routine at every glow-lamp factory, where candle-powers are measured and checked by girls knowing as much of optics as a cow does of the calculus.

#### TRUE RESEARCH WORK NOT LIMITED TO LABORATORIES

"In common parlance, the term 'research' is accorded to any investigations made in a specially equipped laboratory, and by a special staff, while it is refused to, perhaps, more fundamentally original and intrinsically more valuable work carried out in the drawing office or in the works with improvised apparatus. Mr. Little was less eclectic than this in his own use of the term, and included among research workers those ingenious mechanics who have developed agricultural machinery, or such useful devices as the Westinghouse brake and the methods and instruments associated with the electric telegraph. With this view, though it is not the commonly accepted one, we fully agree. A draughtsman who schemes a new layout for a machine shop or a mechanic who 'practicalizes' a machine tool is, in fact, more truly engaged in research work than a chemist who shows, say, that in a certain organic compound one halogen may replace another.

#### GERMANY LEADS IN LABORATORY, NOT IN TRUE INDUSTRIAL RESEARCH

"If, however, the term 'research' be interpreted on this comprehensive basis, we think few will be prepared to concede to Germany the pre-eminence in research which Mr. Little claims for her. Such a claim is defensible only when the term is limited, we might almost say degraded, to cover a laboratory work solely, often partaking largely of a routine character. Undoubtedly much very valuable work has issued from German laboratories, but it can hardly be claimed that any undue proportion of the many great advances made in various departments of applied science during the past few years have thus originated. The Diesel engine, for instance, is balanced by the telephone, and incandescent gas lighting by the electric glow lamp.

#### THE BORN INVESTIGATOR VS. THE PAID FACTORY RESEARCH DEPARTMENT

"It seems to us that research work of value can generally be divided into two classes. In the first place, pioneering researches, in which the man is everything, and the equipment relatively unimportant. Behind these pioneers come, however, a whole army of other investigators, who, by patient and intelligent industry, develop the regions opened by the men of superior genius. Research work of this second kind leads often to very valuable results. It is, however, largely a matter of expenditure and organization, and can almost be bought in the open market, as if it were a material commodity. The labor is very great, so that the credit for the result achieved appertains as much to those bold enough to finance the work as to those who make the actual observations and measurements. Mr. Carnegie was, we believe, the first steel maker in America to employ a works chemist, and he has stated that the venture proved highly profit-

able, since it was found that by purchasing ore by analysis, rather than by reputation, very large economies were realized. No one, however, could contend that great insight into chemical theories and physical facts is needed for the analysis of an iron ore. Care, industry and average intelligence are the main essentials, and such qualities are not specially uncommon, while genius is seldom on sale.

"Though in one part of his address Mr. Little seems to take, as stated, a comprehensive view as to what constitutes research, in much of it he would appear to have most sympathy with the kind that can be organized in a works laboratory, and he makes a special plea for more work of this character. Much undoubtedly can be effected in this way, but how far the system should be extended depends very largely on the nature of the industry involved."

A distinction, frequently made here in America, and found more often in engineering than chemical lines, is indicated by the names Research, Development and Experimental Departments. The Research Department, proper, undertakes the more difficult problems of a broad or general nature without special reference to immediate commercial demand, the solution of which is most obscure and which requires, at least for the direction, men of the rarer sort with natural tendencies toward investigation, born research men. Development Departments, while doing research work also, are primarily concerned with perfection of a process or machine, the general nature of which is known at the start, and which is properly a product of the Research Department, and generally in the form of a patentable invention; the aim is now to find the best form and materials for commercial production and use. The third or Experimental Department merely performs routine tests, the end and aim of which are data for checking specifications of quality or performance, or for detecting those defects of routine factory source which an ordinary factory force can correct: the work of such an experimental department is purely routine, can be learned quickly by anyone and never should be called research at all—though it often is.

Frequently it happens that one establishment cannot afford three such departments so that the work is all thrown into one, variously named. Or, consultants are used to supply the sort of direction required of the first and second or to entirely replace them when the consultant has at command suitable apparatus, equipment and organization, in which case such an independent investigation or research establishment may serve to advantage many individuals in many different industries. It is this sort of thing that is now growing up as a proper bond between the staffs and laboratories of our better mechanical, electrical and chemical engineering schools and the industries with which they are concerned. Much of the best work now being done in this cooperative way by our independent research men or investigators and the industrial establishments is carried on either in the works themselves or in the field outside of the producers' works but without any laboratory proper. The important point here is that the place of doing the work is of no consequence in comparison with the finding of capable men to direct it and keeping them busy to avoid waste of good talent.

#### INDUSTRIAL LABORATORY VALUES AND LIMITATIONS

"We gather that chemists find that in the chemical trades new ideas can be completely and satisfactorily tested in a works laboratory. One of our leading cotton manufacturing firms has also found an organization of this character to be highly profitable, having established many years ago lavishly equipped experimental works in which new ideas are thoroughly investigated. Nothing, however, is published as to the results attained. If a proposed innovation passes satisfactory tests, it is adopted quietly and with as little publicity as possible. As a consequence, when the daily Press expatiates on some remarkable improvement in textile methods as having been recently introduced abroad, it is the case, more often than not, that the identical device has been in commercial operation for years past in the factories of the firm in question. Other British firms pursue a similar policy, carrying out a very large amount of research work of this kind, while saying as little as possible about it. Sheep-dip makers, for instance, investigate, both in their laboratories and on the spot, the life-history and course of development of insect pests from every part of the world, but none of them advertise the fact.

"The organized research laboratory is not, however, so well adapted to the art of engineering as to some other industries, though even here it may unquestionably prove at times quite valuable. Its drawbacks have a twofold origin. In the first place engineering is an art rather than a science. Its exponents are to be classed with other creative minds, and only the routine portion of their work can safely be delegated to others. One of our most progressive engineers has refused for this reason to establish in his works a research laboratory for the solution of such difficulties as may arise. The man who has encountered the difficulties generally knows more about it than he can put in writing, or transfer to another in any other way. He is, therefore, in this engineer's view, the proper man to find the solution, and he is accordingly encouraged to experiment himself. The system in question has proved highly successful, but no doubt there are also cases where certain investigations can properly and conveniently be carried out on the lines advocated by Mr. Little. A striking example of highly valuable work conducted in a factory research laboratory is, in fact, afforded by the history of the tungsten filament lamp. The number of cases in which satisfactory solutions of engineering problems can be found in this way is, however, limited by the circumstances that engineering is concerned quite as much with dynamics as with statics. Laboratory tests may quite easily show the capabilities of a new metallic filament lamp or the value of a new dye-stuff, but in more truly mechanical matters the test of service is often the only really reliable one. The original Lee-Metford rifle, for instance, passed triumphantly through the most searching tests that those responsible for its design could conceive of, but a very few months' service showed that Mr. Thomas Atkins devised without difficulty much more trying ordeals for the weapon, and Mark I. was in consequence very rapidly superseded.

"Most of our large firms take very great precautions to secure the thorough reliability of a new product before definitely placing it on the market. In very many cases, however, it is absolutely necessary that the novelty shall be tested in actual service, and it is not always either convenient or possible to effect this at the maker's works. The machine is, therefore, tested by special arrangement with a customer and is neither listed in a catalog nor otherwise advertised till this, the final test, is completed.

"Considerations of this kind greatly restrict the applicability of organized research work in the field of mechanical engineering, and as one consequence, the openings offered to students from technical colleges are less promising than they are in many other departments of industry. Many such students do indeed find work on the test-beds of manufacturing firms, only to dis-

cover after a year or two that such duties offer no prospect of advancement, and add very little to their knowledge of engineering. In one case, after spending some years at the test-bed of a firm of steam turbine builders, an ex-student had not even learned the essential differences between a reaction and an impulse turbine. Such matters were not included in the curriculum of his college at the date of his graduation, and he added little or nothing to this ignorance by his years of testing."

With some of this we cannot agree, for no matter how poorly the laboratory may serve the purpose of profitable improvement, as is undoubtedly the case in many instances, and no matter how little may be the value of testing work to engineering graduates or to their employers, it does not follow that such considerations greatly restrict the applicability of organized research work in the field of mechanical engineering or in any other branch. The distinction here rests again on names; laboratories as generally understood are not essential to some very useful research nor is the existence of a testing department proof of the doing of research work. Forces of men may spend their lives making consumption tests of turbines, strength tests of metals or determining calorific powers of fuels in well equipped laboratories and improve related industries not one bit, and yet one man with no laboratory whatever may stroll leisurely through a few establishments or sit at his desk and evolve an improvement that may materially advance several industries at once when developed, though before getting it in shape for commercial use experimental development work is almost universally required. Depending on the case, this work may be most profitably done in laboratories, in shop or in the field, but it must be done. The International Harvester Company has added more to improvement of agricultural conditions by its machine and implement developments than any organization in the world, but it has no research laboratory, though maintaining testing and development departments. This does not mean that it does no research, for such results could not be produced without research, only it would be obviously absurd to try to develop standard plows, and tractors to pull them, suitable for every soil in the world by any laboratory tests; the machines must be planned, built and then tried and studied everywhere, then returned to the shops, changed to correct faults and tried again. The real research men here are those who plan and study operation in the plowing field, the only place where it can be studied, and who then analyze faults and plan again; these men spend most of their time in railroad trains rather than in laboratories; in the true sense their laboratory is the plowing field, as it should be.

Americans cannot agree with the idea that the fore-

man or superintendent or engineer, whose primary function is the production, at lowest cost, of goods of proper standard quality, is the best man to carry on research or development work; quite to the contrary, in fact he is the very worst. This is because, first, scheming always occupies the mind to the exclusion of executive routine, which is his main business, and second, but vastly more important, the type of mind and training that best fits for one is destructive, or exclusive, of the other. No man well adapted to pushing routine economic production can possibly discover faults and remedies with efficiency, and certainly the creative mind that can, becomes impatient with production routine and so neglects it.

#### RESEARCH AND THE PROFESSOR

"Experience in research work is often made a *sine qua non* for the holding of a professional chair at certain of our universities, and if the word 'research' be interpreted in a sufficiently liberal and comprehensive manner, the condition is, we think, a wise one. In many cases, however, the conduct of a few experiments on lubrication or on elastic moduli will be counted as research, though the experimenter may have displayed no deep knowledge of engineering and physical principles, and be quite incapable of giving material aid to the advancement of the art. He would, however, on the above basis, be preferred to a competitor who had never made a laboratory experiment in his life, but had been in responsible charge of, say, the bridge department of a large firm.

"On the other hand, there are men of exceptional ability in really original research who have not the gift of commending themselves to students and who fail accordingly to teach anything to any but a few exceptional men. At the same time they may do such good work in the study as to more than outweigh their class room deficiencies so far as the world at large is concerned, unfortunate as matters may be for the average student. It is important that work of this character should be done, but the difficulty is to reconcile the claims of abstract technics with the not unnatural demands of the average British parent. A University should certainly promote the former, but as teaching is also one of its functions, undergraduates have a right to demand that their interests shall not be wholly sacrificed to the claims of research."

It is true that a great many directors of engineering schools have insisted on a research record for newly appointed men without knowing just what they meant by the requirement, and while some still do it, times do change and so do standards. Few enlightened schools now fail to recognize that both teachers and investigators are absolutely necessary on the staff, and while it most commonly happens that ability in one line is inversely proportional to strength in the other, yet we know of quite a number of men who possess this dual power.

C. E. LUCKE

## ORIGINAL PAPERS

### THE BIOCHEMICAL OXYGEN DEMAND OF SEWAGES

By ARTHUR LEDERER<sup>1</sup>

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This paper represents the result of a study of a test to determine the biochemical oxygen demand made

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by a subcommittee of the laboratory section of the American Public Health Association.

Interest in this subject has recently been revived through the adoption of standards of permissible stream pollution by the English Royal Commission on Sewage Disposal, embodied in an appendix of the 8th report of



the commission. The test recommended by the commission will be hereafter referred to as the "English Incubation Test."

Before I go into the details of this test, it seems well to discuss briefly its meaning and importance.

As the title of the paper indicates, the oxygen referred to here is that utilized by microorganisms which take part in the decomposition of sewage. To what extent the reaction taking place is of a purely biological or chemical or physical nature is unknown. The process is most probably a combination of all three forces. In designating properly a test, which gives expression to the demand for oxygen such as is present in streams, one can hardly be criticized for using the expression "Biochemical Oxygen Demand." The danger of introducing the term "Oxygen Demand" alone is that it would be somewhat confusing with the time-honored expression "Oxygen Consumed." We know that "oxygen consumed" indicates the permanganate oxygen required for the oxidation of a small portion of the organic carbonaceous matter. This oxidation is a purely chemical reaction and bears no relation whatsoever to the "biochemical" oxygen demand. The biochemical oxygen demand of a sewage as a rule is much higher than the permanganate oxygen consumption and the figures bear absolutely no relation to each other. In certain cases the biochemical oxygen demand may be low and the permanganate oxygen consumption high. This may occur with trade wastes containing organic carbonaceous preservatives. The principal value of a test for the determination of the biochemical oxygen demand in a sewage lies in the fact that it is the best indicator of what may be called the "strength" of a sewage. Anyone who has ever employed one or the other of such tests is quickly convinced that none of the routine chemical determinations heretofore in use can furnish the same information. From the standpoint of stream pollution it means very little to the sanitary engineer and chemist to know how much organic nitrogen or "oxygen consumed" or chlorine a certain sewage will add to the stream. They are interested in the amount of oxygen that will be absorbed in the stream, particularly during the first stretch after discharge. Of the chemical constituents the suspended matter is of interest because of its relation to the aesthetic features of sewage disposal by dilution, and on account of its relation to the formation of mudbanks. Some instances of comparing the "strength" of certain sewages from the standpoint of the routine chemical analysis and the biochemical oxygen demand are indeed surprising. The writer has in mind one instance in particular, in which a certain sewage when compared to another from the standpoint of the routine chemical tests was twice as strong and when judged by the biochemical oxygen demand about forty times as strong. Personally, I do not advise chemists to disregard chemical determinations in sewages altogether; we surely want to know whether a sewage is alkaline or acid for instance. My principal plea is to subordinate the routine determinations of the chemical constituents to the determination of the oxygen-consuming capacity of a sewage.

The laboratory section of the American Public Health Association has recognized the importance of standardizing such a test and for some months past a subcommittee has devoted its attention to this question. The members of the subcommittee are: F. Bachmann, Chicago; R. H. Brown, New York City; J. W. M. Bunker, Cambridge, Mass.; Frederic Bonnet, Jr., Worcester, Mass.; W. M. Cobleigh, Bozeman, Mont.; John R. Downes, Plainfield, N. J.; F. E. Hale, Brooklyn, N. Y.; C. B. Hoover, Columbus, O.; A. Lederer, Chicago; T. W. Melia, Brooklyn, N. Y.; F. W. Mohlman, Urbana, Ill.; John F. Norton, Boston, Mass.; E. B. Phelps, Washington, D. C.; and S. T. Powell, Baltimore, Md. A. Lederer is chairman of the subcommittee. The following sanitary engineers have been kind enough to give the subcommittee on various occasions the benefit of their valuable opinion: H. C. McRae, Baltimore, Md.; Langdon Pearse, Chicago, Ill.; and W. L. Stevenson, Philadelphia, Pa.

The standardization of a biochemical test differs from the standardization of a purely chemical test in various respects. One chemist might be put to work out a chemical method and his results would be of equal value anywhere. This is not the case with a biochemical test. Two sewages may be alike with reference to their chemical constituents and yet they may differ vastly in their biology. Rarely will two sewages be exactly alike in this respect. No biologic procedure can be expected to furnish ready formulae which would work out with mathematical precision everywhere at all times. Even if we had such a procedure at our disposal we would still have such factors to account for as obstructions in a stream, differences in velocity and temperature, influence of sunlight, absorption of oxygen by mud banks and other factors which of necessity are not represented in a laboratory procedure. It seemed evident, therefore, that in proposing and adopting a standard procedure we would have to confine ourselves for the present to methods furnishing fairly accurate, consistent results, comparable with each other. It could not be expected in the present state of our knowledge of self-purification of rivers with reference to oxygenation and de-oxygenation, that we should be able to work out a procedure which could tell us with certainty how much sewage is to be permitted in a stream to maintain a certain degree of purity further downstream. This could be done only if rivers in all parts of the country were alike with reference to temperatures, velocities, obstructions, etc. Any deeper study of de-oxygenation and oxygenation in a particular stream will apply only to another stream very similar hydrographically. With these conceptions in mind it seemed most advisable to standardize a procedure which would permit the expression of "total biochemical oxygen consumption" and to leave the practical application of this test for the purpose of controlling stream pollution to individual local study.

In order to compare the applicability of a standard procedure in various localities it is important to experiment with as many sewages as possible. Such tests were made with the sewages of Chicago, Ill.,

Plainfield, N. J., Champaign, Ill., Lawrence, Kan., New York City, Washington, D. C. and Worcester, Mass. Since the number of results obtained with Worcester and New York City sewage are too small, these sewages are not considered in connection with this study.

A method of determining the actual strength of putrescible material is given in the last edition of the "Standard Methods of Water Analysis." The method consists in making various dilutions of the putrescible material with aerated tapwater, adding methylene blue as an indicator, and calculating the oxygen demand from the "relative stability" figures obtained. The method is undoubtedly very useful and simple. It will be retained in the next progress report of the committee in a form elaborated upon by Prof. Phelps. The possible objections to this method are that the relative stability figures obtained are based upon empirical findings and that intermediate points of de-oxygenation, if such are desired, cannot be obtained.

The method proposed by the Royal Commission of Sewage Disposal contained much which seemed worthy of a study by American chemists. Briefly, the English procedure is as follows:

A definite volume of sewage or effluent is completely aerated by shaking. It is then mixed with a larger definite volume of tap water and the mixture again aerated. The dilutions recommended for raw sewages and settled sewages are about 99 to 1 and 49 to 1, respectively. The intention is to adjust the ratio of the aerated water to the sewage under test so that during the test only about 50 or 60 per cent of the oxygen in the diluting water will be used up. It is stated that if less than 30 per cent of the initial oxygen is absorbed the error of the experiment becomes large, but if more than 60 per cent is absorbed the error is even greater. A large dilution reduces the food supply of the bacteria and thus retards de-oxygenation. The prepared dilutions are carefully put into 4 clean glass-stoppered bottles holding 11 to 12 ounces. The bottles are left unstoppered for 5 minutes to give the entrapped air at the shoulder a chance to escape. Stress is laid on the importance of having all the liquids in the mixture and even the bottles at incubation temperature before beginning the incubation. The incubation temperature recommended is 65° F. (18.3° C.), this representing the maximum summer temperature of even the most sluggish English streams. The 5-day incubation temperature has been found to give a smaller experimental error than longer incubation periods. Two of the bottles are tested for oxygen at once; the other 2 bottles are tested for oxygen at the end of incubation. The determination of the free oxygen was made by the Winkler method as modified by Rideal and Stewart. The principle of the modification consists in the oxidation of the organic matter and the nitrites by the addition of permanganate in acid solution followed by the addition of 1 cc. of potassium oxalate previous to the addition of the standard reagents employed in the Winkler method. The English standard for sewage effluents

is one that absorbs less than 20 p. p. m. of oxygen in 5 days at 65° F.

It is not the purpose of this subcommittee to concern itself with the adoption of standards for sewage effluents but solely to fix a laboratory procedure which will give uniform results. It is thought that such a procedure will be a valuable aid to the sanitary engineer in establishing standards of permissible stream pollution.

There were a number of features in the original English test for the determination of the biochemical oxygen demand which did not appeal to the collaborators, and after considerable correspondence it was finally decided to do some comparative work with the method, employing, however, an incubation temperature of 20° C., and to extend the incubation period to 10 days in order to study the oxygen consumption from day to day. The assumption was that the oxygen consumption at the end of 10 days would be practically 100 per cent. It was also decided to work with three different concentrations simultaneously, so that the influence of concentration upon oxygen consumption could be studied. An ideal experimental series was to show oxygen absorptions of less than 30 per cent, between 30 and 60 per cent, and over 60 per cent, respectively. The preparation of the mixtures previous to incubation differed from the English procedure in that we employed aerated distilled water instead of tap water and 8-ounce bottles were used instead of 11-ounce bottles. The sewage was not aerated before mixing it with the distilled water, but the mixture was brought to the incubation temperature previous to incubation. The sewage was settled in the laboratory before the mixtures were prepared, for the reason that unevenly divided suspended matter might have introduced serious discrepancies in the final results. The original Winkler method was employed for the determination of the free oxygen. Later on, during the tests, it was recommended to employ Hale and Melia's modification of the Winkler method. Professor Phelps employed Rideal and Stewart's modification in the latter part of his series. A number of blue-printed record sheets were mailed to the co-workers in order to facilitate the compilation of the results obtained. It was suggested at the start that each collaborator should obtain at least 10 ideal series, but the time and labor involved was so great that it was impossible to live up to it. Unless one has worked with the same sewage for a considerable period it is almost impossible to prepare dilutions which will allow reductions of oxygen simultaneously to 30 per cent, to between 30 and 60 per cent and over 60 per cent. A great deal of time in such work is always lost with preliminary tests. In order to obtain an ideal series one has to incubate at least 30 bottles and preferably more in order to check doubtful results.

In his series, Mr. Mohlman recorded in addition to the oxygen consumption figures, Phelps' velocity coefficient "K" for each day. A subsequent calculation of K on all of the results obtained by the various collaborators gave some interesting information. The

TABLE I—PERCENTAGE OF TOTAL OXYGEN ABSORBED AND PHELPS' VELOCITY COEFFICIENT, K, AFTER 24 HOURS AND 5 DAYS INCUBATION AT 20° C. Total Oxygen Consumption Compared with Initial Available Oxygen after 10 Days Incubation

Date of sampling 1914	LESS THAN 30 PER CENT						30 to 60 PER CENT						MORE THAN 60 PER CENT					
	24 hours		5 days		K Average of 10 days incubation	24 hours		5 days		K Average of 10 days incubation	24 hours		5 days		K Average of 10 days incubation			
	% O abs'd	K	% O abs'd	K		% O abs'd	K	% O abs'd	K		% O abs'd	K						
SERIES: Phelps. SOURCE: Screened Washington Sewage																		
April 21.....												34	0.00052	78	0.00030	0.00032		
22.....												23	0.00031	76	0.00027	0.00025		
24.....	23	0.00031	75	0.00020	0.00020	23	0.00026	67	0.00015	0.00017								
28.....	28	0.00026	61	0.00016	0.00018	26	0.00026	80	0.00019	0.00019								
29.....						29	0.00037	77	0.00021	0.00022								
30.....	38	0.00031	84	0.00015	0.00017													
	22	0.00018	88	0.00016	0.00016													
	20	0.00018	80	0.00016	0.00017													
May 1.....	17	0.00018	65	0.00016	0.00016	33	0.00034	85	0.00020	0.00018								
						32	0.00037	77	0.00019	0.00019								
						25	0.00030	75	0.00021	0.00021								
12.....	18	0.00018	52	0.00013	0.00014	30	0.00043	86	0.00030	0.00029								
13.....	17	0.00013	60	0.00012	0.00011	37	0.00042	75	0.00019	0.00019								
						15	0.00015	81	0.00020	0.00017								
14.....	47	0.00039	63	0.00010	0.00016	28	0.00042	88	0.00021	0.00023								
						41	0.00045	90	0.00024	0.00025								
15.....	30	0.00031	86	0.00010	0.00018							34	0.00064	76	0.00037	0.00040		
16.....						27	0.00043	79	0.00028	0.00028								
						23	0.00035	89	0.00030	0.00027								
23.....						26	0.00034	77	0.00024	0.00023								
						23	0.00034	83	0.00028	0.00024								
25.....						20	0.00024	71	0.00020	0.00021								
						21	0.00028	79	0.00025	0.00021								
26.....												34	0.00054	84	0.00037	0.00036		
28.....												36	0.00056	85	0.00035	0.00036		
												36	0.00057	80	0.00033	0.00036		
												46	0.00071	92	0.00038	0.00039		
SERIES: Young and Bruckmiller. SOURCE: Settled Sewage—Lawrence, Kansas																		
May 23.....	25	0.0024	69	0.0015	0.0015	51	0.0060	51	0.0012	0.0020		63	0.0070	23	0.0027	0.0031		
26.....	27	0.0024	74	0.0016	0.0016	50	0.0013	67	0.00079	0.00079		53	0.0062	68	0.0018	0.0025		
27.....	14	0.0015	29	0.00049	0.00094	51	0.0058	65	0.0016	0.0022		59	0.0065	80	0.0021	0.0026		
June 9.....						45	0.012	77	0.0046	0.0054		38	0.0031	87	0.0019	0.0020		
						33	0.0052	76	0.0027	0.0031								
10.....	28	0.0015	77	0.0020	0.0018	38	0.0060	52	0.0017	0.0026		30	0.0024	89	0.0020	0.0018		
11.....	29	0.0034	41	0.00096	0.0016	58	0.0068	90	0.0023	0.0025		61	0.0060	77	0.0016	0.0020		
SERIES: Downes. SOURCE: Screened Sewage—Plainfield, N. J.																		
May 2.....	18	0.0011	66	0.00075	0.00087	23	0.00086	67	0.00057	0.00060								
						44	0.0014	84	0.00062	0.00064								
15.....	26	0.0011	84	0.00082	0.00080	35	0.0010	71	0.00045	0.00052								
						35	0.00094	78	0.00051	0.00054								
26.....	37	0.0014	84	0.00066	0.00057							44	0.0016	81	0.00072	0.00068		
												57	0.0018	89	0.0011	0.0010		
June 1.....	37	0.0012	86	0.00060	0.00059							44	0.0015	79	0.00070	0.00077		
6.....												28	0.0013	73	0.00059	0.0011		
12.....						45	0.0012	84	0.00050	0.00058		41	0.0014	70	0.00062	0.00075		
SERIES: Mohlman. SOURCE: Crude and Septic Sewage—Champaign, Ill.																		
Septic																		
April 21.....												34	0.0020	81	0.0013	0.0013		
												27	0.0021	75	0.0014	0.0015		
21.....												25	0.0014	80	0.0013	0.0014		
												18	0.0013	76	0.0015	0.0014		
25.....												14	0.0010	64	0.0011	0.0011		
30.....						15	0.0016	56	0.0014	0.0014		25	0.0017	72	0.0012	0.0012		
						17	0.0013	58	0.0010	0.0011		18	0.0010	86	0.0015	0.0011		
Crude																		
May 5.....						38	0.0045	76	0.0017	0.0020								
						26	0.0036	66	0.0021	0.0021								
5.....						17	0.0017	65	0.0015	0.0016		25	0.0014	82	0.0014	0.0015		
9.....						26	0.0060	61	0.0031	0.0036		22	0.0035	61	0.0026	0.0028		
11.....						34	0.0058	60	0.0020	0.0025		25	0.0072	73	0.0052	0.0053		
14.....						24	0.0058	60	0.0020	0.0025		14	0.0049	58	0.0025	0.0031		
						28	0.0079	55	0.0032	0.0040								
SERIES: Lederer and Bachmann. SOURCE: Crude Sewage (Settled)—Chicago, Ill.																		
April 20.....	26	0.0012	78	0.00084	0.00088	16	0.00046	80	0.00051	0.00047								
	18	0.00059	76	0.00052	0.00049													
21.....	28	0.0011	72	0.00057	0.00069	37	0.00074	74	0.00032	0.00036								
	26	0.00070	78	0.00045	0.00046													
22.....	10	0.00036	78	0.00068	0.00055	11	0.00036	66	0.00043	0.00040								
						22	0.00043	81	0.00040	0.00043								
23.....	24	0.0011	66	0.00063	0.00062	30	0.00086	70	0.00045	0.00046								
						33	0.00075	76	0.00039	0.00042								
28.....	41	0.0011	91	0.00047	0.00049	25	0.00051	75	0.00037	0.00038								
	35	0.00069	91	0.00041	0.00039													
29.....	22	0.00071	71	0.00044	0.00050													
	24	0.00056	68	0.00032	0.00036													
30.....	44	0.0016	83	0.00066	0.00077	31	0.00069	92	0.00048	0.00041								
						42	0.00075	79	0.00032	0.00040								
May 1.....	33	0.0010	84	0.00059	0.00058	24	0.00062	82	0.00048	0.00049								
						26	0.00060	82	0.00048	0.00049								
4.....	29	0.0016	79	0.00089	0.00084	29	0.00082	90	0.00058	0.00058		33	0.00089	93	0.00067	0.00061		
6.....	41	0.0016	94	0.00080	0.00088	26	0.00057	76	0.00039	0.00040								
						31	0.00062	94	0.00049	0.00051								
27.....	30	0.00071	60	0.00031	0.00040	24	0.00032	79	0.00025	0.00023								
	30	0.00039	78	0.00022	0.00021													
28.....	35	0.0012	65	0.00047	0.00055	33	0.00075	90	0.00051	0.00047		33	0.00096	81	0.00075	0.00065		
June 4.....	41	0.0011	91	0.00050	0.00053	24	0.00059	88	0.00059	0.00050		19	0.00047	83	0.00070	0.00066		

factor K is part of a formula developed by Prof. Phelps and Col. Black during an investigation of the pollution of New York harbor in 1911. The method employed by Phelps and Black consisted in the incubation of suitable mixtures of the sewage with

aerated water for a specified time, say 24 hours. The oxygen is determined at the start and at the end of incubation. Considering the reaction between the organic matter of the sewage and the oxygen dissolved in the water, the following relation is said to hold:



$\log \frac{O'}{O} = KCt$ .  $O'$  represents the initial,  $O$  the final amount of oxygen present.  $C$  expresses the concentration of the sewage,  $t$  the duration of the incubation in hours, and  $K$  the velocity constant of the reaction to be determined. Knowing the form of the reaction curve, one computes first  $K$  and then by extrapolation to an extended period the total oxygen demand of the organic matter in the sewage. Originally it was claimed that  $K$  is independent of the extent of dilution. This, however, was found later to be not quite correct. It was my experience

at the highest concentration of the sewage. After 24 hours,  $K$  is much higher than after 2 days and it decreases (this does not show in the tables given) continuously up to the last day of incubation. However, after the fourth or fifth day the differences are by no means as marked as they are during the first few days. In many cases,  $K$  is fairly constant after 5 days.  $K$  after 5 days of incubation coincides quite well with the average of the 10 days period.

These results are given without comment or recommendation, for the reason that the formula is now undergoing a very comprehensive study in connection with

TABLE II—PER CENT RELATION OF "MG. OXYGEN ADDED TO 1 LITER OF SEWAGE" TO "MG. OXYGEN ABSORBED PER LITER OF SEWAGE" AFTER 24 HOURS, 5 DAYS AND 10 DAYS INCUBATION AT 20° C.

DATE	COLLABORATOR	Mg. O Per added cent to 1 l. dilution	PER CENT O ABSORBED IN					DATE	COLLABORATOR	Mg. O Per added cent to 1 l. dilution	PER CENT O ABSORBED IN					
			24 hours	5 days	10 days	Av.	Av.				24 hours	5 days	10 days	Av.	Av.	
May 14	Mohlman	0.25	3488	10	20	20	36	April 20	Lederer and Bachmann	3.0	280	7	35	43		
23	Young and Bruckmiller	0.36	2111	5	14	21		21		287	11	23	31			
26			2111	2.5	18	24		May 6		280	10	9	28	29	37	
26			2111	5	14.5	20		April 21	Mohlman	282	28	66	80			
27			2111	2.5	5	18		21		276	21	68	87			
June 10			2111	2.5	18	24		30		276	15	70	82			
11			2111	7	4	9	13	22	21.5	275	21	21	69	68	84	
5	Mohlman	0.50	1680	9.5	26	34		May 5	Downes	352	21	21	40	40	47	
9			1512	15	35	57		15		252	19	43	54			
11			1580	18	51	70		26		225	30	55	69			
14			1688	16	15	26	34	45	51	226	28	54	63			
12	Downes		2132	3	10	16		June 1		230	26	66	90			
21			2080	3.5	3	11	10	15		223	23	26	33	51	65	
May 21	Young and Bruckmiller	0.72	1055	20	20	46		April 22	Lederer and Bachmann	210	9.5	36	44			
26			1055	20	26	40		23		215	15	35	45			
27			1055	21	28	42		May 27		202	9	20	28			
June 9			1055	19	42	55		28		210	15.5	43	48			
10			1055	21	32	55		June 4		202	12	12	46	36	52	43
11			1055	24	21	37	31	41	46.5	224	6	20	27			
May 26	Downes	1.00	938	7	16	5	20		June 4	Phelps	222	6	16	25		
June 1			959	7	16	18	19		May 8		224	4	16	25		
April 30	Mohlman		856	8	31	55		13		217	4	16	25			
30			854	7	24	41		12		210	4	13	25			
May 5			884	22	38	57		13		221	4	12				
5			836	9	51	74		14		219	8	11	17.5			
14			728	18	50	82		15		221	7	19	22			
April 20	Lederer and Bachmann		826	24	15	50	38	86	62	228	9	27	34			
21			870	7	21	26		June 16		219	7	6	28	32	26	
22			870	6	15	20		April 30	Lederer and Bachmann	5.0	166	13	40	36	45	
23			870	2	17	22		May 1		168	19	36	45			
28			890	6	16	24		4		168	15	58				
28			870	6	13	14		June 12	Downes	166	22	17	60	45	65	55
29			860	3.5	12	16		May 6	Lederer and Bachmann	6.0	150	84	96			
30			880	8	17	20		April 24	Phelps	146	37	45	64	79	92	94
May 1			880	6	17	20		28		135	18.5	55	55	59	59	
4			870	8	22	28		29		147	8	22	33			
6			860	8	20	20		30		146	9	20	39			
27			840	4	12			May 1		147	11	30				
28			870	7	13	20		8		148	6	24				
June 4			840	6	13	16	14	19		146	11	28	33			
April 30	Lederer and Bachmann	1.5	573	5	20	25		13		139	5	27	36			
23	Young and Bruckmiller	1.8	586	6	5.5	17	18	21	23	146	11	27	35			
26			422	50	73	79		13		141	13	27	35			
26			422	46	59	87		14		143	13	30	48			
June 9			422	26	61	70		23		144	14	32	42			
10			422	21	63	71		27		141	10	10	37	28	44	38
11			422	45	39	57	63	73	77	111	11	38	49			
15			530	9	27	40		June 4	Lederer and Bachmann	7.0	111	11	77	94		
April 21	Mohlman		512	12	10.5	22	24	30	35	111	17	19	74	63	90	78
20			429	20	55	73		May 8	Phelps	8.0	107	13	38	50		
21			409	14	58	75		12		101	17	49	57			
25			372	11	46	70		13		102	6.5	36	44			
30			430	17	15	48	52	67	71	109	18	41	45			
23	Lederer and Bachmann		425	3.5	21	32		15		103	25	58	73			
23			435	9	6	22	21	31	31	108	10	36	51			
30	Phelps		422	2	8			25		104	11	82	43	53	53	
May 5			437	1	1.5	8	11	11		87	25	56	72			
April 28	Lederer and Bachmann	2.5	340	9	25	27		May 22		82.5	16	52	69			
29			336	7	20	30		26		82	26	64	76			
30			344	9	28	30		28		83	26	62	72			
May 1			344	8	34	34		28		80	32	25	65	60	75	
4			340	11	9	33	26	36	31							

that  $K$  decreased as the concentration increased, and the results obtained in Tables I and II bear this out uniformly. To meet this objection, Phelps recommended that  $C$  in his formula be effected by a concentration exponent  $n$ , which would have to be determined for each particular sewage by a study of a series of dilutions.

In making a study of  $K$ , obtained in the experiments of the collaborators, the following facts present themselves very strikingly.  $K$  is almost invariably lowest

the work of the U. S. Public Health Service on the self-purification of the Ohio and Potomac rivers. Possibly, the results obtained in connection with the investigation of the English incubation test will be of some service to the students of the formula.

Before discussing the results obtained by the collaborators and giving their comments, the results are compiled in Table I.

In some cases, as can be noted, the number of determinations was rather small, and in such cases one

is hardly justified in drawing an average. The heading "Per Cent of Total Oxygen Absorbed" serves to indicate the per cent ratio of absorption, assuming that it is 100 per cent after 10 days. For instance, the column "Per Cent Oxygen Absorbed in 24 Hours" indicates the per cent ratio between the oxygen absorbed in 24 hours and 10 days.

Table II shows the per cent of oxygen absorbed after 1, 5 and 10 days incubation.

Table I shows very strikingly that the rate of absorption in certain dilutions with certain sewages is fairly uniform but that there is no uniformity whatsoever in this respect when comparing different sewages with each other. In other words, one might incubate a certain dilution of a certain sewage for 24 hours and assume with fair certainty the approximate oxygen consumption in 5 days and 10 days, provided he has once established the relation in preliminary tests. This, of course, implies a good deal of work which the busy works-chemist is not always in a position to do.

In all of the experiments, the number of mg. of oxygen absorbed per liter of sewage was lower the higher the concentration. The percentage of oxygen absorbed by the sewage increased with the concentration.

Some experiments were omitted in the tabulation, for the reason that there was a discrepancy in the results which apparently seemed illogical. Such discrepancies were noted in nearly all of the series. There is no doubt that some of these discrepancies are not merely analytical errors but due to reasons which still lack satisfactory explanation. It often happened that the oxygen consumption would suddenly increase on one day, to drop down to a logical figure on the next day. The greater part of the consumption has been reached as a rule by the fifth day. The consumption between the fifth and tenth day amounted to about 20 to 25 per cent of the total. On the whole the concentration did not matter greatly when comparing the per cent oxygen absorbed in 24 hours and 5 days (Table I). When the incubation was such that less than 30 per cent and between 30 and 60 per cent of the initial oxygen was consumed, the "per cent oxygen absorbed in 24 hours" was about 30 per cent (variation 17 to 46), and the "per cent oxygen absorbed in 5 days" about 75 per cent of the total (variation 58 to 81). When more than 60 per cent of the initial oxygen was absorbed, the ratio of absorption was somewhat higher. For the 1-day period the ratio was on the average 35 per cent (variation 22 to 51) and for the 5-day period, about 80 per cent of the total per cent consumption (variation 73 to 86). That this method furnishes only approximate figures at the best is apparent.

Some of the collaborators have given a more detailed opinion on the result of their tests, excerpts of which are given herewith.

Mr. Mohlman, who employed Jackson's bulb pipettes as seals for the bottles during incubation, states that "A number of runs were spoiled by variations in incubation temperature." Instead of preparing the required dilutions for each individual bottle, Mr. Mohlman prepared a larger quantity of the desired mixture

and siphoned the solution into the 8-ounce bottles. (The procedure has been employed by the writer on previous dilution tests and seems much simpler and quicker than preparing individual mixtures. If carefully done, there need be no additional aeration and this procedure has the advantage of furnishing an absolutely uniform liquid.) "The most striking conclusion is the variability in the amount of oxygen used by the undiluted sewage, as it varies in every case directly with the amount added and is always higher in the higher dilutions."

Dr. Hale writes: "The parts per million of oxygen absorbed obtained with different dilutions by the English method do not agree. As such a result is not reasonable, instead of carrying out more series, we began to investigate immediately as to the cause of these discrepancies. We have found that aerated distilled water, even though not saturated when put into bottles and incubated at either 20 or 37° C., loses a certain amount of oxygen which varies with the temperature, with the initial oxygen, and with the type of the stopper. We have tested the rubber bulbs, rubber stoppers, glass stoppers, open bottles, and open tubes (Phelps) and found varying losses. We believe that oxygen collects under the stopper and upon the introduction of solutions for testing is forced out of the bottle and lost. This occurs whenever the oxygen in the bottle has not been exhausted. Such a correction would then apply to all determinations made by the English method, but as the correction is very uncertain, it makes the English method very unreliable and my conclusions at present are that the dilution method is the only reliable standard, that the English method cannot be recommended unless extensive experiments find a way of eliminating this uncertainty"..... "There is also another reason why the English method is unreliable and that is that different amounts of sewage require different lengths of time to reach the endpoint, consequently if such a method is adopted we shall have to choose a certain dilution, say one per cent, and determine the length of time it takes that dilution to reach completion, besides eliminating previous error of loss of oxygen that I have mentioned. It may be that by filling bottles and allowing them to stand in the incubator for three days before the addition of sewage, the error may be eliminated, since the loss appeared to be constant in two to three days. This means, however, a troublesome procedure."

Mr. Downes feels that efforts should be abandoned to secure absolute oxygen capacity figures. "On the other hand, I feel that we should work towards the shortest incubation period which will give compatible results indicative of the effect of the sewage in question on the stream which it is to enter. In plant and stream control the value of the results increase in proportion to the speed with which they can be obtained. I suggest a 24-hour period for routine work as best adapted to our American needs. From past experience I had been led to hope that I could show that such a period was more independent of the dilution than longer periods. This I have not been able to do to my satisfaction. On the other hand, results for 24-hour tests

are just as compatible and just as reliable as results from longer periods. In cases when a comparatively stable condition of the sample has been reached between the fifth and tenth day without exhaustion of the available oxygen, the 24-hour results are about 40 per cent of the whole." . . . . "It seems that we can hardly do better than to adopt a dilution that will leave a 30 per cent to 60 per cent residual oxygen in 5 days as the English do, for it is certain that too high a concentration would interfere with the life of the oxidizing organisms."

Mr. Hoover would prefer the term "dissolved oxygen consumed" to "biochemical oxygen demand."

Prof. Phelps finds the work not very satisfactory and it is his intention to develop some method which will take us entirely away from oxygen determinations.

Notwithstanding the shortcomings of the method, it is of some advantage to be able to know even approximately the 24-hour and total oxygen consumption of the sewage. As long as we lack proven methods which will give us this information accurately, the introduction of the "Modified English Incubation Test" as a provisional method at the next annual meeting of the American Public Health Association ought to serve some useful purpose. A method developed by me for the determination of the oxygen demand consists in the addition of saltpeter, the oxygen of which is utilized during incubation just as the oxygen in diluting water is used. The method has been published in the May number of the *Journal of Infectious Diseases*. The method has since been simplified by me and has given satisfaction in determining the strength of sewages in polluted waters. Various chemists are employing the method at present and their criticism and results will help to decide whether the method is of sufficient value to supplant the one discussed at length in this paper, or whether it is to serve as a matter of choice. It is also to be hoped that Prof. Phelps will be successful in his endeavor to originate a reliable method for the determination of the oxygen demand and the ratio of oxygen absorption.

It is the intention to present the provisional procedure as the "Modified English Incubation Test" for the determination of the biochemical oxygen demand in the following form:

"A definite volume of sewage or effluent is mixed with aerated distilled water or tap water, free from nitrites and nitrates, in such proportion that between 30 and 60 per cent of the available oxygen is consumed at the end of 10 days incubation at 20° C. Care should be taken to store the diluting water for some time (one or two days) at the constant temperature of 20° C., previous to the preparation of the mixture. The sewage and even the bottles which are to be incubated should be of the same temperature to obtain satisfactory results. The sewage may be added directly into the bottles or else a larger quantity of the mixture may be prepared and the mixture siphoned into the bottles, care being taken to avoid aeration. A bottle of 250 cc. capacity with a seal such as is often used for the methylene blue putrescibility test is employed. It is necessary to establish the ratio of ab-

sorption in a definite concentration for each particular dry weather flow sewage before resorting to short time incubation. Having established the per cent ratio of absorption for 1, 5 and 10 days at the proper concentration at various times, it may then suffice to incubate the mixture for 24 hours at 20° C. The results after incubation of 24 hours can be converted into approximate results obtainable after 5 and 10 days incubation by multiplying by the proper factors. It is assumed that a 10-day period of incubation coincides with the complete oxidation of the sewage mixture, which is correct for all practical purposes. Results should be expressed in "milligrams of oxygen absorbed per liter of crude sewage or effluent." For purposes of comparison with other sewages, it is desirable to state the oxygen consumption in milligrams for 24 hours and 10 days. The 10-day consumption figure may either be actually determined or obtained by calculation with the factor established in the initial experiments."

The writer wishes to thank heartily all those who have cooperated in this work by actual experiment and by suggestions. On the whole, the results of the experimental work have not been very satisfying to the collaborators, including myself. Even though we did not decide on a method which promises to be of a permanent character, I feel that we shall be able at least to obtain more uniform results by establishing a standard concentration, incubation temperature and period. If all those who are interested sufficiently in this test will establish the approximate ratio of oxygen exhaustion in their sewage during a 10-day period, the results obtained in various places ought to be fairly comparable with each other.

THE SANITARY DISTRICT OF CHICAGO  
39TH ST. AND LAKE FRONT

## NOTES ON THE COMPOSITION OF MIDCONTINENTAL PETROLEUM<sup>1</sup>

By F. W. BUSHONG  
Received August 14, 1914

The crude oil from which the products described herein were derived came from the wells of the Alluwe Oil Company in Oklahoma. It is a typical Oklahoma oil of specific gravity  $2.08513$  at  $15^{\circ}/15^{\circ}$ .

Although the writer is firmly convinced that a thorough series of fractional distillations begun on a factory scale and carried out to the highest limit of efficiency would richly reward the immense labor involved by opening up a new world of possibilities in the way of chemical products to be manufactured from petroleum he keenly feels his helplessness in the face of the enormity of such an undertaking. The time at his disposal permitted only a series of four distillations.

Two 8-liter portions of the crude oil were subjected to distillation from a copper retort until the temperature of the vapors reached  $315^{\circ}$  C. The distillates were collected in 10 fractions of 5 per cent each by volume. The redistillations were carried out in Jena

<sup>1</sup> This work was done under the J. R. Greenlees Temporary Industrial Fellowship, established under the direction of the late Dr. Robert Kennedy Duncan, in the University of Kansas, 1908.

<sup>2</sup> There was a loss of gasoline during shipment. The oil at the well is lighter.



glass flasks. In the case of the gasoline fractions a LeBel-Henninger dephlegmator was employed. Twelve-degree fractions were collected in the second distillation, four-degree fractions in the third, and two-degree fractions in the fourth. Natural gas was used as the source of heat in the first three distillations, but in the final distillation electricity was employed in the following manner: The distilling flask was mounted upon an electric flask heater which was so regulated as to heat the oil nearly to its boiling point. A coil consisting of about five meters No. 24 German silver wire was held in place in the form of a ring within the distilling flask by means of two stout copper wire terminals which passed up through the cork stopper in the neck of the flask. The quantity of current passed through this coil in order to effect the distillation of the preheated oil was small, and was controlled by outside resistance. This arrangement permitted easy control and constancy of distillation, and did not require a great difference between the temperature of the heating coil and that of the oil.

Tables I and II show the fractions thus collected, their relative quantities, densities and indices of refraction.

TABLE I—GASOLINE FRACTIONS

Fraction	Bar. pr. mm.	Percentage by vol.	Sp. gr. 15°/15°	Ref. index 15° C.
Below 40°	739	0.5	0.6296	1.3616
40 to 50°	739	0.12	0.6448	1.3675
50 to 60°	739	0.35	0.6608	1.3750
60 to 62°	739	0.08	0.6806	1.3806
62 to 64°	744	0.08	0.6806	1.3828
64 to 66°	744	0.10	0.6806	1.3847
66 to 68°	744	0.34	0.6867	1.3873
68 to 70°	744	0.29	0.6926	1.3898
70 to 72°	744	0.27	0.6976	1.3921
72 to 74°	744	0.22	0.6976	1.3946
74 to 76°	740	0.18	0.6976	1.3965
76 to 78°	740	0.07	0.6976	1.3987
78 to 80°	740	0.19	0.7171	1.4006
80 to 82°	740	0.13	0.7211	1.4023
82 to 84°	740	0.11	0.7221	1.4029
84 to 86°	740	0.11	0.7261	1.4042
86 to 88°	740	0.36	0.7260	1.4051
88 to 90°	740	0.31	0.7273	1.4056
90 to 92°	740	0.26	0.7286	1.4063
92 to 94°	740	0.44	0.7291	1.4068
94 to 96°	740	0.39	0.7306	1.4080
96 to 98°	740	0.93	0.7331	1.4093
98 to 100°	740	0.31	0.7364	1.4113
100 to 102°	731	0.41	0.7391	1.4120
102 to 104°	731	0.29	0.7407	1.4133
104 to 106°	731	0.28	0.7430	1.4143
106 to 108°	731	0.13	0.7432	1.4144
108 to 110°	731	0.15	0.7436	1.4147
110 to 112°	731	0.31	0.7440	1.4153
112 to 114°	731	0.29	0.7438	1.4150
114 to 116°	731	0.36	0.7433	1.4151
116 to 118°	731	0.36	0.7435	1.4152
118 to 120°	744	0.37	0.7443	1.4159
120 to 122°	744	0.43	0.7450	1.4162
122 to 124°	744	0.46	0.7467	1.4185
124 to 126°	744	0.34	0.7485	1.4195
126 to 128°	744	0.40	0.7526	1.4217
128 to 130°	744	0.35	0.7557	1.4238
130 to 132°	744	0.32	0.7600	1.4258
132 to 134°	748	0.24	0.7617	1.4267
134 to 136°	748	0.35	0.7652	1.4283
136 to 138°	750	0.31	0.7666	1.4297
138 to 140°	750	0.27	0.7679	1.4300
140 to 142°	750	0.22	0.7684	1.4307
142 to 144°	750	0.33	0.7679	1.4300
144 to 146°	750	0.40	0.7682	1.4299
146 to 148°	750	0.14	0.7686	1.4299
148 to 150°	750	0.22	0.7687	1.4300

TOTAL GASOLINE 13.77

Results of analysis of some of the untreated heavier kerosene fractions are here shown:

Fraction	Per cent C	Per cent H	Per cent O (dif.)
290 to 292°	86.07	13.31	0.62
292 to 294°	85.96	13.03	1.01
294 to 296°	86.24	13.18	0.58
296 to 298°	85.80	13.06	1.14

AVERAGE..... 86.02 13.14 0.84

Fractions dried by means of metallic sodium, and filtered, were found to have the following composition:

Fraction	Per cent C	Per cent H
252 to 254°	86.58	13.41
272 to 274°	86.39	13.43
292 to 294°	86.65	13.46
296 to 298°	86.29	13.26

Several fractions were treated with ozone, in the cold. After separating the resinified ozonides, by settling, the residual oils had the following composition:

Fraction	Per cent C	Per cent H	Per cent O (dif.)
302 to 304°	84.19	13.13	2.68
300 to 302°	83.88	12.88	1.4338
298 to 300°	83.73	13.31	2.96
296 to 298°	84.54	13.35	2.11
Same after drying with Na	84.84	13.67	1.49

The residual oil from the 302 to 304° fraction, after refining with successive portions of concentrated

TABLE II—KEROSENE FRACTIONS

Fraction	Bar. pr. mm.	Percentage by vol.	Sp. gr. 15°/15°	Ref. index 15° C.
150 to 152°	738	0.20	0.7715	1.4320
152 to 154°	738	0.50	0.7730	1.4330
154 to 156°	739	0.36	0.7744	1.4338
156 to 158°	739	0.49	0.7762	1.4350
158 to 160°	739	0.31	0.7784	1.4359
160 to 162°	739	0.55	0.7800	1.4372
162 to 164°	737	0.60	0.7818	1.4384
164 to 166° (a)		0.37	0.7844	1.4393
166 to 168°	744	0.36	0.7849	1.4391
168 to 170°	738	0.40	0.7868	1.4405
170 to 172°	733	0.36	0.7885	1.4418
172 to 174°	733	0.52	0.7897	1.4425
174 to 176°	733	0.35	0.7910	1.4430
176 to 178°	736	0.44	0.7920	1.4435
178 to 180°	736	0.36	0.7930	1.4440
180 to 182°	736	0.24	0.7944	1.4447
182 to 184°	735	0.44	0.7957	1.4450
184 to 186°	735	0.20	0.7969	1.4458
186 to 188°	734	0.48	0.7980	1.4466
188 to 190°	734	0.40	0.7997	1.4470
190 to 192°	734	0.51	0.8006	1.4478
192 to 194°	734	0.32	0.8026	1.4485
194 to 196°	734	0.30	0.8030	1.4492
196 to 198°	734	0.30	0.8035	1.4498
198 to 200°	734	0.33	0.8064	1.4505
200 to 202°	731	0.43	0.8075	1.4508
202 to 204°	738	0.51	0.8094	1.4518
204 to 206°	738	0.38	0.8105	1.4523
206 to 208°	738	0.47	0.8119	1.4530
208 to 210°	738	0.43	0.8129	1.4538
210 to 212°	736	0.51	0.8138	1.4544
212 to 214°	736	0.33	0.8154	1.4550
214 to 216°	733	0.51	0.8160	1.4552
216 to 218°	733	0.28	0.8175	1.4559
218 to 220°	733	0.40	0.8184	1.4563
220 to 222°	732	0.50	0.8190	1.4570
222 to 224°	730	0.38	0.8207	1.4579
224 to 226°	730	0.45	0.8219	1.4583
226 to 228°	730	0.41	0.8230	1.4592
228 to 230°	730	0.33	0.8244	1.4601
230 to 232°	730	0.41	0.8252	1.4607
232 to 234°	730	0.37	0.8264	1.4611
234 to 236°	742	0.40	0.8270	1.4617
236 to 238°	742	0.40	0.8290	1.4627
238 to 240°	742	0.42	0.8306	1.4632
240 to 242°	742	0.42	0.8322	1.4644
242 to 244°	742	0.34	0.8329	1.4651
244 to 246°	741	0.30	0.8339	1.4658
246 to 248°	741	0.31	0.8355	1.4662
248 to 250°	741	0.39	0.8360	1.4670
250 to 252°	741	0.51	0.8381	1.4675
252 to 254°	741	0.24	0.8388	1.4684
254 to 256°	740	0.39	0.8398	1.4690
256 to 258°	740	0.40	0.8410	1.4698
258 to 260°	740	0.34	0.8418	1.4700
260 to 262°	738	0.37	0.8434	1.4708
262 to 264°	738	0.46	0.8440	1.4721
264 to 266°	737	0.45	0.8455	1.4729
266 to 268°	737	0.27	0.8462	1.4732
268 to 270°	737	0.44	0.8469	1.4738
270 to 272°	735	0.23	0.8480	1.4741
272 to 274°	735	0.41	0.8483	1.4745
274 to 276°	733	0.38	0.8483	1.4745
276 to 278°	733	0.43	0.8595	1.4747
278 to 280°	736	0.33	0.8595	1.4750
280 to 282°	741	0.33	0.8598	1.4750
282 to 284°	741	0.28	0.8533	1.4761
284 to 286°	741	0.28	0.8540	1.4765
286 to 288°	741	0.40	0.8508	1.4754
288 to 290°	740	0.28	0.8508	1.4754
290 to 292°	740	0.29	0.8510	1.4756
292 to 294°	739	0.37	0.8513	1.4755
294 to 296°	739	0.22	0.8518	1.4760
296 to 298°	739	0.28	0.8525	1.4760
298 to 300°	739	0.28	0.8530	1.4760

(a) Mercury column of thermometer became shattered.

sulfuric acid, washing in the usual manner and drying over calcium chloride, gave the following analysis:

85.81 per cent C and 13.99 per cent H

The residual oil of the 300 to 302° fraction (after separation of the ozonide) was refined by means of liquid sulfur dioxide, according to the method of Edeleanu.<sup>1</sup> The oil thus refined, washed and dried, had the refractive index 1.4712 at 14°, and was found to contain

Calculated for $C_{17}H_{30}$	85.42 per cent C	14.12 per cent H
	85.62 per cent C	14.38 per cent H

The oil extracted therefrom by the liquid sulfur dioxide, after washing, etc., had the refractive index 1.5222 at 16° and contained

82.42 per cent C	10.31 per cent H	7.27 per cent O (dif.)
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The 296 to 298° fraction, weighing 58.34 g. after treatment with sodium, and filtration, was treated in the cold with ozonized air for five successive days. The ozonide was washed with about 25 cc. of light gasoline, to which it gave only a slight color. After evaporation of the residual gasoline in a current of natural gas there remained 5.8 g. of ozonide—10 per cent of the weight of oil. Some of this ozonide was treated with anhydrous ether, yielding a red colored solution, which was poured off from a brick-red insoluble powder. After the evaporation of the ether there remained a transparent red syrup which hardened slowly like a varnish. A portion for analysis was spread in a film over the inner surface of a porcelain boat and dried in a desiccator. Its weight became constant at 0.4122 g. On combustion this gave 0.9623 g.  $CO_2$  and 0.2336 g.  $H_2O$ .

Found	63.67 per cent C	6.34 per cent H
Calculated for $C_{17}H_{30}O_6$	63.72 per cent C	6.30 per cent H

29.98 per cent O

This is in accordance with the results obtained by Molinari and Fenaroli<sup>2</sup> with distillates from Roumanian and Russian petroleum.

The 252 to 254° fraction—the largest of the upper kerosene—after drying over sodium, was refined with liquid sulfur dioxide.

A.—The refined oil had a specific gravity of 0.8240 at 15° and the refractive index 1.4660 at 15°. Its composition was found to be

85.29 per cent C	13.98 per cent H
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B.—The sulfur dioxide extract, after washing, etc., had the refractive index 1.5412 at 12° and the composition

88.94 per cent C	10.19 per cent H	0.87 per cent O
Calculated for $C_{15}H_{26}$	89.93 per cent C	10.07 per cent H

(dif.)

This extract, B, was then treated with ozonized oxygen, in the cold. It yielded an ozonide which when freshly precipitated was flaky and almost white, but slowly resinified. It was taken up in absolute ether and shaken with successive portions of a dilute aqueous solution of potassium hydroxide until freed from acids. It was then washed, and dried over calcium chloride. After evaporation of the ether a thick resinous syrup remained. 0.4681 g. of the dry substance gave 1.2712 g.  $CO_2$  and 0.2884 g.  $H_2O$ .

Found	74.06 per cent C	6.89 per cent H
Calc. for $C_{15}H_{26}O_8$	73.73 per cent C	6.61 per cent H

19.66 per cent O

Molinari and Fenaroli isolated from the petroleum

<sup>1</sup> U. S. Pat. 911,553, Feb. 2, 1909; *Chem. Abs.*, **3**, 1082.

<sup>2</sup> *Berichte*, **41** (1908), 3407.

of Velleja, Italy, a flaky white ozonide having the composition  $C_{15}H_{16}O_8$ , which they believe to have been formed from the hydrocarbon  $C_{15}H_{16}$  by the addition of two  $O_3$  groups to two double bonds. Possibly our original product also may have been the same double ozonide, which on treatment with alkali lost half of its oxygen.

In the excellent work "Wissenschaftliche Grundlagen der Erdölbereitung," by Dr. L. Gurwitsch, Berlin, 1913, pp. 34–35, the significance of the suggestion of Molinari and Fenaroli regarding the preëxistence of hydrocarbons of the series  $C_nH_{2n-14}$  in kerosene is critically discussed, and it is pointed out that oxidation may precede the ozonide formation. The analysis of the sulfur dioxide extract of the unoxidized 252 to 254° fraction shows approximately the same hydrogen content as the hydrocarbon  $C_{15}H_{26}$ . Since, however, the extraction method cannot effect complete separation of the two classes of hydrocarbons it is very probable that this extract may consist essentially of the hydrocarbon  $C_{15}H_{16}$ , contaminated by small residual quantities of ordinary naphthenes.

The ozone reaction has given us a valuable working tool for detecting new constituents of petroleum.

The extraction method of Edeleanu enables us to remove these constituents from the main body of the petroleum, in concentrated form and apparently unaltered condition.

In the opinion of the writer, however, the proof of the chemical composition of these reactive constituents awaits the development of an independent method of attacking the problem.

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## EFFECT OF PRESSURE ON YIELDS OF PRODUCTS IN THE DESTRUCTIVE DISTILLATION OF HARDWOOD

By R. C. PALMER

Received August 5, 1914

### INTRODUCTION

A study of the effect of pressure on yields was conducted at the Forest Products Laboratory as a part of a series of experiments to devise methods of increasing the amounts of valuable products obtained in the destructive distillation of hardwoods.

It is generally known that certain primary reactions occur in the action of dry heat on wood substance in the absence of air, resulting in the primary products: acetic acid, methyl alcohol, a very complex tar, charcoal, and such gases as carbon dioxide, carbon monoxide and methane. From a theoretical standpoint, it is possible to produce secondary reactions between these primary products such as  $2CH_3COOH = CH_3COCH_3 + CO_2 + H_2O$ , resulting in a decrease in acetic acid, or  $CH_3OH + CH_3COOH = CH_3COOCH_3 + H_2O$ , giving a decrease in both alcohol and acetic acid.

The decomposition reactions of wood which result in the formation of tar are at present too little understood even for speculation but undoubtedly a relation exists between the tar and charcoal, both products containing a high carbon content,<sup>1</sup> and a relation between acid or alcohol and tar is certainly not impossible.

<sup>1</sup> Ultimate analysis of birch tar has been given as  $C_{10}H_{10}O_4$ . Klason, *Arch. f. Kemi Min. and Geol.*, Vol. **8**, No. 7.

## METHOD OF MAKING EXPERIMENTS

**APPARATUS**—A diagrammatic sketch of the apparatus used is shown in Fig. 1. This apparatus is a cast iron autoclave with walls 1 inch thick to withstand high pressure. The autoclave has a jacket

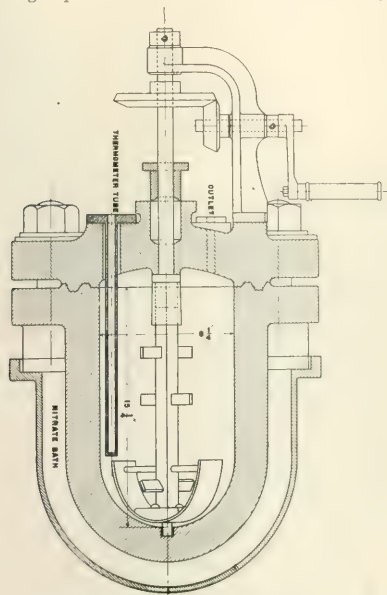


FIG 1—EXPERIMENTAL AUTOCLAVE

filled with a heating medium. The heat is supplied by means of a giant Bunsen burner. A mixture of sodium and potassium nitrates was found to be a convenient bath material. A stirring device was provided for keeping the charge well mixed. It was found necessary to stir continuously during the exothermic reaction in order to secure check runs under any given conditions of pressure and size of chip.

The temperature of the distillation was measured at a point as near the center of the charcoal residue as the stirrer would permit. In order that the reaction should be uniformly complete in all cases, the distillation was considered finished when the constant maximum temperature was maintained for 10 minutes with constant stirring. A final temperature of as near to 335° C. as possible was attained in each distillation.

In heating up the retort with air alone it was found that the temperature in the retort was constantly about 100° lower than the bath temperature, probably due to large conduction of heat through the heavy wall. Therefore, in making distillations, the bath was raised to about 450° C. and maintained at that temperature throughout the experiment.

**OPERATION OF RETORT**—Distillations were made using: (1) sawdust of two species, maple and birch; (2) chips averaging 1 by 1/8 by 1/8 inch of birch. For distillations in the autoclave the small material was selected because differences due to different qualities of material could be obviated. The objections to the

use of small material because of difficulties in heating were avoided by stirring the charge. Also while probably not commercial in the ordinary types of distilling apparatus, sawdust or chips served the purpose of obtaining simply comparative results.

The different kinds of material were first distilled at atmospheric pressure under conditions as far as possible comparable with the ordinary methods of commercially distilling wood. Distillations were then made under different pressures up to 150 lbs. per sq. in. In the pressure distillations as soon as the first water distillate was coming in sufficient quantity to insure that all air had been displaced the outlet was closed until the desired pressure was obtained as indicated on a pressure gauge, the outlet then being opened just enough to maintain the pressure.

In most cases very little manipulation of the outlet valve was necessary to secure constant pressure conditions throughout the run except at the very last, when the quantity of distillate was very small. A typical data sheet is shown in Table I, which indicates the manner of making the distillations.

TABLE I—BIRCH CHIPS

Run No. 43, February 7, 1914.				Weight charge, 2903 g. Oven dry weight, 2621 g.	
Time	Temperature °C.		Pressure Lbs.	Total distillate Cc.	REMARKS
	Autoclave	Bath			
8.30 A.M.					
9.39	116	363			
9.51	155	400	60		
9.57	179	415	60	100	
10.02	194	425	60	200	
10.06	209	429	60	300	Tar started
10.09	225	435	60	400	
10.11	242	440	60	500	
10.13	250	442	60	600	
10.15	272	442	60	700	Stirred continuously
10.16	286	443	60	800	
10.17	298	444		900	
10.18	311	447	60	1000	
10.23	325	450	60	1100	
10.27	331	452	60	1130	Gas off
10.30	335	452	60	1155	
10.33	338	445	60	1162	
10.37	338		60	1166	Kept on stirring
10.40	337		60	1168	
12.20 P.M.	220		0	1197	
				Total, 1229	

## RESULTS

**RELATION BETWEEN TIME, TEMPERATURE, AND PER CENT OF DISTILLATE**—Figs. 2 and 3 show the relation between time, temperature, and per cent of total distillate for typical distillations made at 0, 60, and 120 lbs. pressure. Distillations were usually complete within two hours after the distillate began coming over. It is evident from the temperature distillate curve that the temperature was not the true average temperature of the autoclave but only served as an indication of the rate of rise of the temperature.

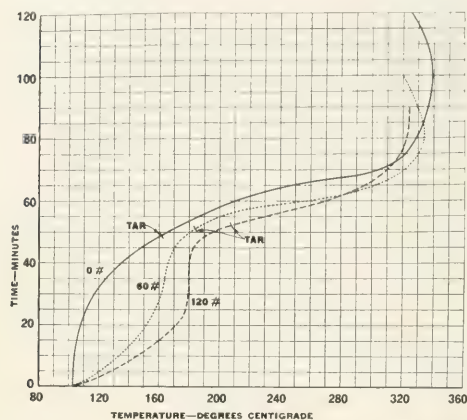
Free tar began coming over in the distillate after about the same lapse of time in each case, but at 160° for 0 lbs., 180° for 60 lbs. and about 210° C. for 120 lbs. pressure. From numerous other experiments by the author and from the reports of other investigators the destructive distillation point accompanied by the formation of free tar occurs at about 275° C. at atmospheric pressure. The thermometer reading is, therefore, evidently too low during the distillation stage. However, since with air alone the thermometer could not be raised within 100° of the bath, and since the final temperature was in nearly all cases about 100° lower



than the bath, the final indicated temperature was probably more nearly correct. No allowance is made for the heat developed by the exothermic reaction of distillation but with only about 3000 g. of wood this would not be very great.

In spite of the uncertainty of having measured the actual temperature the following effects of pressure or the manner of distillation are indicated:

I—The decided difference in the temperature-time and temperature-per cent distillate curves with



FIGS. II AND III—RELATION BETWEEN TEMPERATURE, TIME AND PERCENTAGE OF TOTAL DISTILLATE

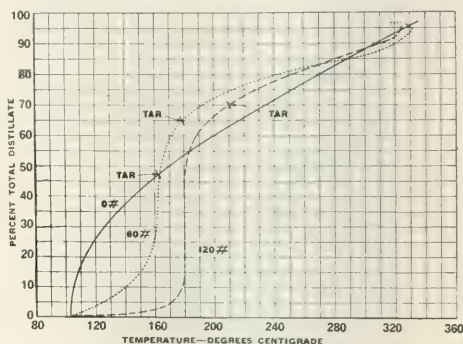
increasing pressures is probably due entirely to the increase in boiling point of water under pressure. At 60 lbs. pressure, water boils at 155° C.; at 120 lbs. pressure, at 176° C. The flattening out of the curves for these pressures occurs very close to these points.

II—The destructive distillation point as indicated by the formation of tar takes place at a higher temperature with increasing pressure.

III—The higher the pressure the more distillate is obtained before tar is formed during destructive distillation. The moisture content of the charge in

tar. The results obtained from different forms of wood and different species are given in Table II. The results in each case are the average of at least three consistent distillations.

The alcohol yields from chips are decidedly higher than for sawdust of the same material. This was about the most important difference of chips over the smaller form and the cause is probably the size of the material. Distillations on 80-lb. charges of wood 18" long and 3" × 3" cross section from which



these chips and sawdust were taken gave 1.54 per cent alcohol. The same thing held true for maple. Sawdust gave lower yields of alcohol compared to large forms of wood.

The effects of pressure on the products of destructive distillation were independent of the form and species used and were in general as follows:

ACETIC ACID—Increased pressure tended to decidedly decrease the yield of acetic acid, the average effect of distilling at 120 lbs. over 0 lb. being a decrease of about 25 per cent. In the case of maple sawdust

TABLE II—EFFECT OF PRESSURE ON DESTRUCTIVE DISTILLATION (Results in percentages of oven dry weight of material)

MATERIAL	Pressure Lbs.	Acid	Alcohol	Charcoal	TAR		Concentration of dissolved tar in distillate	Per cent pyro acid minus moisture	Gas	Gas, tar and charcoal	Tar and charcoal
					Dissolved	Total					
Maple sawdust	0	5.89	1.09	38.93	3.74	8.04	9.05	35.0	25.2	72.17	46.97
	60	4.81	1.18	41.49	1.33	3.23	3.49	28.8	30.3	75.02	44.72
	150	4.10	1.08	42.46	0.97	2.67	2.72	27.66	29.36	74.49	45.13
Birch sawdust	0	6.76	1.15	37.2	5.28	11.98	8.53	36.37	19.70	68.98	49.18
	60	5.34	1.23	40.38	1.40	4.25	2.93	29.95	25.10	69.73	44.63
	120	5.20	1.25	42.07	1.12	3.86	2.71	29.84	25.55	71.48	45.93
Birch chips	0	6.32	1.42	36.61	12.55	16.96	24.4	42.64	16.03	69.60	53.57
	60	5.61	1.50	39.5	6.29	11.70	12.1	34.23	20.13	71.33	51.20
	120	5.44	1.53	40.48	5.64	9.08	8.75	32.90	21.21	70.77	49.56

the typical cases drawn would not account for this difference as the 0 and 120 lb. runs were 18.9 per cent and 19.1 per cent moisture, respectively, while the 60 lb. run was 25.4 per cent moisture.

EFFECT OF PRESSURE ON PRODUCTS—The distillate from each run was allowed to stand until all free tar had settled out and the clear pyroigneous acid had separated. Both acid liquor and settled tar were then weighed and measured. The crude pyroigneous acid was analyzed for acid, alcohol, and dissolved

at 150 lbs. the yield of acid was 28 per cent less than at 0 lb.

ALCOHOL—Up to 120 lbs. the effect of pressure was to increase slightly the yield of alcohol, about 8 per cent more alcohol being obtained at this pressure over 0 lb.

Three-quarters as much increase, or 6 per cent, was obtained with 60 lbs. pressure. In the case of maple sawdust at 150 lbs. the yield was practically the same as at 0 lb., indicating that above 120 lbs. the effect

of pressure is to decrease rather than increase the yield of alcohol. This was also substantiated by a number of preliminary distillations.

**CHARCOAL**—At 60 lbs. pressure, 8 per cent more charcoal was obtained than at 0 lb., and at 120 lbs. there was an increase of 11 per cent over atmospheric distillations.

**DISTILLATE**—The clear pyroligneous acid, independent of moisture content of wood, was decreased about 20 per cent under 60 lbs. pressure but had only small further decrease at 120 lbs. or 150 lbs.

**GAS**—There was a similar but reverse effect on the gas (determined by difference). At 60 lbs. pressure there was about 25 per cent more gas than at 0 lb., but 120 or 150 lbs. only gave very little more gas or even less than 60 lbs. (maple sawdust at 150 lbs. gave 2 per cent less than at 60 lbs.).

**TAR**—The most decided effect of distilling under pressures greater than 0 lb. was on the tar. At 60 lbs. the yield of total tar (tar which settled out of the distillate plus tar dissolved in the crude pyroligneous acid) was 60 to 65 per cent less than at 0 lb. and at 120 lbs. and 150 lbs. pressure about 68 per cent less.

This same effect was even more apparent on the dissolved tar alone. A decrease of as much as 75 per cent at 150 lbs. over 0 lb. being obtained for maple sawdust. The high yield of tar from birch chips as compared to sawdust was probably due to the fact that the chips were very dry. Other work on a much larger scale has given the same effect using very dry wood.

#### RELATION BETWEEN GAS, TAR, AND CHARCOAL

It seemed probable that some relation might be established between gas, tar, and charcoal, and this has been indicated in Table II. Any such relation is not very marked, however, although the sum of the three products is fairly constant.

It is of interest to compare these results with some recent work of Klason<sup>1</sup> who has studied the effects of distilling birch under pressures lower than atmospheric, a pressure of 0.01 mm. being maintained even during the gas stage by immersing the receiver in liquid air. In brief, the same tendencies were obtained, viz., the higher the pressure (in this case atmospheric compared to pressures of 0.01 mm.) the more alcohol and charcoal were obtained and less tar, but Klason reported practically no effect on the acetic acid.

#### SUMMARY

I—Destructive distillations of birch and maple were made on a small scale to study the effect of pressures greater than atmospheric on the yields of products.

II—In general, the effect of destructively distilling wood under increasing pressure is to increase the alcohol slightly when moderate pressures are used and to increase the charcoal and gas. Further effects were to decrease the acetic acid, the pyroligneous liquor, and tar.

III—The effects of 60 lbs. pressure over 0 lb. are much more decided on all products than the effects of increasing the pressure beyond 60 lbs.

IV—The most decided effect of pressure was on the tar. At 60 lbs. pressure this product was decreased 60 to 65 per cent.

V—From a practical standpoint, the most interesting effect of pressure is in connection with the yield of soluble tar.

Distillations were made at pressures as high as 450 lbs., but the exothermic reaction was so violent that it was not advisable to continue the experiments. At this pressure, the concentration of the dissolved tar in the pyroligneous acid was so low that redistillation was not necessary in order to titrate the distillate—or in practical operation the first distillation of the primary liquor would not be necessary in order to make gray acetate of lime. It is possible that pyroligneous acid free from soluble tar might be obtained by subjecting the distillate to a high pressure during the vapor stage but the application of this result is not yet apparent.

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### OILS OF THE CONIFERAE: III. THE LEAF AND TWIG AND THE CONE OILS OF WESTERN YELLOW PINE AND SUGAR PINE

By A. W. SCHORGER

Received October 1, 1914

The leaf oil of western yellow pine (*Pinus ponderosa*, Laws.) has apparently never been examined chemically. Brown<sup>1</sup> in 1901 briefly described a plant in Oregon operating on the needles of *Pinus ponderosa*, the products obtained being oil and fiber. A ton of the needles produced ten pounds of oil, equivalent to a yield of 0.50 per cent of oil, which is considerably larger than the yield obtained from the California trees.

#### LEAF AND TWIG OILS OF WESTERN YELLOW PINE

The oils varied in color from bright yellow to green. When exposed to the light for two or three days the yellow oils also acquired a green color. Some oils showed a green fluorescence.

#### FRACTIONAL DISTILLATION OF THE LEAF OIL OF WESTERN YELLOW PINE

Boiling point, °C.	Per cent
161-165	10
165-170	64
170-185	9
185-250	12.5
185-185 (35°mm.)	3

#### PHYSICAL AND CHEMICAL CONSTANTS OF THE OILS OF WESTERN YELLOW PINE

Nos. 2173-2443 distilled from needles only; 2497-2560, from needles and twigs

Sample No.	Sp. gr.	Ref. index 15° C.	$\alpha_D^{20}$	Acid No.	Ester No.	Ester No. after action	Percentage		
							Acetate	Free alcohol	Yield
2173	0.8762	1.4815	-15.73	2.36	4.02	27.58	1.41	6.60	0.040
2174	0.8718	1.4812	-17.30	1.87	5.70	24.11	2.00	5.13	0.040
2384	0.8729	1.4794	-18.72	1.15	5.15	34.18	1.80	8.16	0.037
2385	0.8750	1.4793	-18.62	1.58	6.71	34.15	2.35	7.75	0.072
2386	0.8739	1.4789	-17.47	1.73	7.11	32.52	2.49	7.12	0.066
2387	0.8747	1.4797	-18.62	1.58	3.88	26.19	1.36	6.24	0.097
2403	0.8784	1.4807	-18.72	2.11	5.94	35.10	2.08	8.20	0.058
2404	0.8849	1.4832	-16.81	1.28	5.15	28.81	1.80	6.62	0.115
2442	0.8722	1.4802	-17.82	0.88	7.65	28.79	2.68	5.91	0.095
2443	0.8765	1.4808	-19.59	0.85	7.83	31.97	2.74	6.76	0.074
2497	0.8793	1.4805	-17.26	0.87	6.32	35.68	2.21	8.08	0.126
2498	0.8838	1.4837	-17.02	0.84	8.10	30.59	2.84	6.29	0.122
2499	0.8844	1.4838	-16.77	0.67	5.89	31.58	2.06	7.20	0.124
2560	0.8755	1.4812	-15.94	0.73	6.73	25.14	2.35	5.14	0.084

$\alpha$ -PINENE—The oil contains but a small amount

<sup>1</sup> Scientific American, 84 (1901), 344.

<sup>1</sup> "Experiments on the Dry Distillation of Wood," Peter Klason, *Arch. f. Kemie Min. and Geol.*, Vol. 5, No. 7.

of  $\alpha$ -pinene, since after repeated fractionation only 7.25 g. (1.5 per cent) were obtained between 157 and 160°. The oil had a specific gravity of 0.8660 at 15° and the optical rotation  $\alpha_{D23} = -27^\circ$ . A small yield of pinene nitrosochloride melting at 102.5° was obtained.

Camphene was not detected in the portion b. p. 160–163°.

**$\beta$ -PINENE**—The oil consists largely of  $\beta$ -pinene, 375 g. (75 per cent) boiling between 160–170°, mainly between 164–167°. The fraction boiling at 166° had the specific rotation  $\alpha_D = -19.87^\circ$ . After oxidizing 150 g. of the oil with alkaline potassium permanganate, 76 g. of oil were recovered by steam distillation, while the oxidation liquor yielded 27.5 g. of sodium nopinate, equal to a yield of 37.2 per cent based on 74 grams of oxidized oil. The free nopinic acid melted at 126°. By further oxidation the ketone nopinone was obtained, the semicarbazone of which melted at 188°.

**DIPENTENE**—The oil boiling between 170–180° amounted to 33 g. (6.6 per cent). The fraction b. p. 170–175°,  $\alpha_{D20} = -11.90^\circ$ , yielded a dihydrochloride melting at 50°. The fraction b. p. 175–180°,  $\alpha_{D22} = -11.83^\circ$ , gave a tetrabromide melting at 124°.

**BORNEOL**—The oil boiling between 205–250° was saponified and the portion b. p. 205–217°,  $\alpha_{D25} = -17.68^\circ$ , heated with phthalic anhydride. The phthalic ester was purified in the usual way. On saponification and steam distillation a small amount of oil was recovered. On oxidizing the oil with Beckmann's reagent solid camphor was obtained. The amount of camphor was too small for recrystallization. After sublimation it melted at about 160°. The material had the appearance and odor of camphor and showed the property of the latter substance of rotating when dropped on water.

**"GREEN OIL."**—On distillation at 35 mm. pressure 15.5 g. (3.1 per cent) of oil distilled between 155–185°. The oil was greenish yellow in color and had:  $d_{15} = 0.9270$ ;  $\alpha_{D26} = -8.39^\circ$  for a 56 per cent solution in ether. No solid derivations were obtained. It gave the usual color reactions for "green oil."

**ACIDS**—The oil previous to distillation was extracted with sodium carbonate. Acetic and formic acids were found to be present in the extract by means of their silver salts. These acids were also obtained by hydrolysis of the esters.

#### CONE OIL OF WESTERN YELLOW PINE

The oil had the following properties: Color, light green;  $d_{15} = 0.8757$ ,  $n_{D15} = 1.4780$ ,  $\alpha_{D20} = 11.48^\circ$ , acid No. 1.27, ester No. 7.20, ester No. after acetylation 22.41, yield of oil 0.063 per cent.

Boiling point, °C.	Per cent
164–170	57
170–195	29
195–250	3.5
250–290	3.5

**FURFURAL**—The aqueous extract from the first fraction gave a strong color reaction for furfural when treated with aniline and hydrochloric acid.

**$\alpha$ -PINENE**—The  $\alpha$ -pinene fraction b. p. 159–164°,  $\alpha_{D25} = -25.33^\circ$ , amounted to 7.8 g. (6.3 per cent).

Pinene was identified by means of the nitrosochloride melting at 103°.

**$\beta$ -PINENE**—On oxidation of the fraction b. p. 164–170°,  $d_{15} = 0.8639$ ,  $\alpha_{D22} = -18.62^\circ$ , with alkaline  $KMnO_4$  sodium nopinate was obtained. The free nopinic acid melted at 126–127°. The total  $\beta$ -pinene fractions amounted to 74.2 g. (60 per cent).

**DIPENTENE**—Two fractions, amounting to 15.8 g. (12.8 per cent), were collected between 170–176°. The fraction b. p. 170–173°,  $\alpha_{D20} = -6.40^\circ$ , was examined for phellandrene with negative results. Dissolved in dry ether and saturated with dry  $HCl$  gas, the oil gave a good yield of dihydrochloride melting at 50°.

**BORNEOL**—The ester fraction was too small for examination. The free alcohol and ester content have been calculated as borneol and bornyl acetate.

**"GREEN OIL"**—The oil boiling between 250–290° was dark green in color and weighed 4.08 g. (3.3 per cent). A crystalline hydrochloride was not obtained.

#### LEAF AND TWIG OILS OF SUGAR PINE

The color of the oils of the sugar pine (*Pinus lambertiana*, Dougl.) ranged from pale lemon-yellow to dark reddish yellow and light green to greenish yellow.

Boiling point, °C.	Per cent
158–165	40
165–170	29
170–186	18
186–210	1
210–250	9

**FURFURAL**—This aldehyde was qualitatively detected in the first fractions.

**$\alpha$ -PINENE**—The fraction examined for  $\alpha$ -pinene had: b. p. 156–158°,  $d_{15} = 0.8645$ ,  $\alpha_{D24} = -10.16^\circ$ . A good yield of pinene nitrosochloride, m. p. 103°, was obtained. The nitropiperidine melted at 119°. The total  $\alpha$ -pinene fractions, b. p. 156–160°, weighed 89.5 g. (20.7 per cent).

**$\beta$ -PINENE**—The  $\beta$ -pinene fractions amounted to 51 per cent and distilled largely between 164 and 167°. Oxidation of 100 g. of oil having a b. p. of 164–167°,  $d_{15} = 0.8680$ ,  $\alpha_{D25} = -15.73^\circ$ , with alkaline  $KMnO_4$

PHYSICAL AND CHEMICAL CONSTANTS OF THE OILS OF SUGAR PINE

Sam- ple No.	Sp. gr. 15° C.	Ref. index 15° C.	$\alpha_{D20}$	Acid No.	Ester No.	Ester after acetyl- ation	Acetate	Free alco- hol	Yield of oil
2175	0.8738	1.4794	-11.07	2.38	4.04	28.46	1.41	6.84	
2405	0.8703	1.4777	-16.50	1.34	2.22	29.68	0.78	7.71	0.045
2406	0.8710	1.4779	-16.18	1.44	3.55	32.04	1.24	8.01	0.052
2409	0.8676	1.4794	-15.52	0.68	4.51	24.35	1.58	5.54	0.098
2413	0.8686	1.4795	-15.49	0.97	5.91	23.25	2.07	4.84	0.097
2469	0.8705	1.4790	-11.83	1.06	5.42	29.27	1.90	6.68	0.110
2470	0.8695	1.4785	-12.70	1.02	4.19	28.49	1.47	6.81	0.120

gave 12 g. of sodium nopinate, 64 g. of oil being recovered by steam distillation. The free nopinic acid melted at 126° and the nopinone semicarbazone at 188.5°.

**DIPENTENE**—Bromination of a fraction b. p. 174–178°,  $d_{15} = 0.8581$ ,  $\alpha_{D29} = -22.17^\circ$ , gave a tetrabromide melting at 124°. The dihydrochloride of the fraction b. p. 170–174° melted at 50°, indicating the absence of sylvestrene. The total dipentene fractions amounted to 52.4 g. (12 per cent).



**BORNEOL**—The fraction b. p. 205–235° was saponified, distilled with steam, and heated with phthalic anhydride. On saponification of the phthalic ester and distillation with steam an oil first passed over followed by a very small amount of solid borneol. On oxidizing, the oil camphor melting at 167–170° was obtained. An alcoholic solution of the camphor was *l*-rotatory.

**COMBINED ACIDS**—The acids obtained by saponification of the esters were precipitated in three fractions containing 35.27 per cent, 40.80 per cent and 64.86 per cent silver. The silver content of the fractions shows that acetic acid is present along with a higher fatty acid or acids.

**"GREEN OIL"**—About 1 per cent of "green oil" was obtained from the residue after removal of the esters, and appeared to be identical with the high-boiling fraction occurring in other needle oils.

#### CONE OIL OF SUGAR PINE

The oil and the following properties: Color, light green;  $d_{15}^0$  0.8692,  $n_{D15}^0$  1.4771,  $\alpha_{D20}^0$  -23.18°, acid No. 0.63, ester No. 3.75, ester No. after acetylation 17.04, yield of oil 0.318 per cent.

Boiling point, ° C.	Per cent
159.5–165	64
165–170	19
170–194	11
194–230	2.5
230–253	1
255–290	1

**FURFURAL**—Furfural was qualitatively detected in the first fraction.

**$\alpha$ -PINENE**—The fraction b. p. 155–159°,  $d_{15}^0$  0.8646,  $\alpha_{D17}^0$  -30.62°, gave a nitrosochloride melting at 98–99°. The pinene nitropiperidine melted at 116° after three crystallizations from alcohol and a fourth crystallization did not raise the melting point. The total  $\alpha$ -pinene fractions amounted to 57.5 g.

**CAMPHENE**—The camphene fractions distilled as follows: (1) b. p. 160–161°, weight 21.5 g., (2) b. p. 161–163°, weight 33.9 g.,  $d_{15}^0$  0.8683,  $\alpha_{D17}^0$  -26.42°. Fifty grams of the oil were treated with glacial acetic acid-sulfuric acid mixture. From the reaction product 6.5 g. of crystalline isoborneol were recovered. After repeated crystallization the isoborneol melted at 211–212° in a sealed tube.

**$\beta$ -PINENE**—The  $\beta$ -pinene fractions amounted to 104.5 g. (39.43 per cent). It boiled between 163–170° and had:  $d_{15}^0$  0.8688,  $\alpha_{D17}^0$  -22.65°. On oxidation a yield of 35 per cent of sodium nopinate was obtained. The free nopinic acid melted at 126°. Five grams of sodium nopinate on further oxidation yielded 1.6 g. ofopinone whose semicarbazone melted at 188–188.5°.

**DIPENTENE**—The fraction b. p. 170–180°,  $\alpha_{D17}^0$  -15.10°, amounting to 4.4 per cent gave a dihydrochloride melting at 49–50°.

**ESTER FRACTION**—The portion b. p. 194–230°, after saponification, was too small for further examination. The free alcohol and ester content have been calculated as borneol and bornyl acetate.

Between 255–290°, 1 per cent of a yellow oil was obtained that appeared to be a sesquiterpene. On dis-

solving the oil in ether and saturating with HCl gas the solution turned purple. A crystalline hydrochloride was not obtained.

#### SUMMARY

The percentage composition of the leaf and twig and cone oils is approximately as follows:

	WESTERN YELLOW PINE		SUGAR PINE	
	Leaf and twig oil	Cone oil	Leaf and twig oil	Cone oil
Furfural	Trace	Trace	Trace	Trace
1- $\alpha$ -Pinene	2	6	21	21
1-Camphene	75	60	51	39
1- $\beta$ -Pinene	6	12–13	12	4–5
Dipentene	2	2.5	1.5	1.5
Ester as bornyl acetate	7	4	8	1
Free alcohol (1-borneol)	3	3–4	1	1
"Green oil"	5	10	7	7
Sesquiterpene(?)				
Losses				

FOREST PRODUCTS LABORATORY  
FOREST SERVICE, DEPARTMENT OF AGRICULTURE  
(In Cooperation with the University of Wisconsin)  
MADISON

#### THE EFFECT OF RESENE ON THE LATHERING OF SOAP SOLUTIONS<sup>1</sup>

By CHAS. H. HERTY AND C. W. WILLIARD

The total annual production of rosin on a conservative estimate is not less than 2,500,000 barrels of 500 lbs. each. Not less than half of this rosin is used in the manufacture of soap. The reason for its use in this industry lies in the fact that the acids of the rosin readily form alkali salts which are very soluble in water, hydrolyze readily and form solutions which lather freely when agitated.

But rosin contains on an average, approximately 7 per cent of "resene" or unsaponifiable matter. As this resene possesses none of the properties which make rosin valuable for soap-making it must be considered as a filler. According to the above figures therefore, from 40,000,000 to 45,000,000 lbs. of this filler, resene, go into soap annually.

Is it true that resene is to be regarded simply as a filler in soaps? May it not have some positive action, either prejudicial or beneficial? A search of the literature failed to show any recorded experiments on this subject and conversations with chemists of soap works failed to elicit any very definite convictions on the subject. In view of the large amount of this material annually used it seemed desirable, therefore, to carry out some experiments to determine this point. The line selected was the effect of resene on the lathering of soap solutions.

#### PREPARATION OF RESENE

The resene used in these experiments was prepared as follows: 1200 g. of the oleoresin of *Pinus heterophylla* (Cuban or slash pine) were dissolved in 9 liters of *N/2* alcoholic potash and the solution allowed to stand 18 hrs. After filtering, water was added almost to precipitation and the solution extracted three times by shaking out thoroughly with petroleum ether, boiling below 70° C. Eight liters of the petroleum ether were used in each extraction. The three extracts were combined and shaken out with 10 liters of 50 per cent alcohol, in order to remove dissolved po-

<sup>1</sup> Presented at the 48th Meeting of the American Chemical Society, Rochester, September 8–12, 1913.

tassium salts of resin acids. The extract was then concentrated by distillation until the temperature of the escaping vapors of petroleum ether reached 65° C. The concentrated residue was again shaken out with 50 per cent alcohol and subjected to steam distillation in order to remove the spirits of turpentine and residual petroleum ether. The resene, mixed with water from condensed steam, was dissolved in petroleum ether (boiling up to 50° C.), separated from the water layer by a separatory funnel, again washed with 50 per cent alcohol as a final precaution against dissolved potassium salts, and the petroleum ether evaporated, at first spontaneously, then for a short time on a steam bath with constant stirring: 65 g. of resene, an amber colored, very viscous mass, resembling well strained honey, were obtained.

#### ANALYSES OF SOAPS USED

Three different types of soap were used throughout the experiments; toilet, castile and cheap laundry. These soaps analyzed<sup>1</sup> as follows:

TABLE I RESULTS IN PERCENTAGES

Soap	Starch	Moisture	Inert mineral matter	Total alkali	Fatty acids
Toilet	None	19	None	8.57	70
Castile	None	19	15	5.60	60
Laundry	None	23	30	5.00	40

#### EXPERIMENTAL

With each of the three soaps mentioned above two solutions were prepared, one by dissolving 5 g. of the soap in distilled water to a volume of 250 cc.; the other by dissolving 5 g. of the soap and 0.14 g. of resene in 250 cc. of alcohol, in order to secure uniform mixing of the soap and resene, evaporating the alcohol on a steam bath, and dissolving the residue in water to a volume of 250 cc. In all of the experiments described below 5 cc. portions of these solutions were diluted with the necessary amount of distilled water, the solutions placed in salt-mouth bottles provided with well ground glass stoppers and the bottles, two at a time, the one containing simply the soap solution, the other the soap plus resene solution, were placed on a double shaking apparatus, such as is commonly employed in making milk-shakes. These were given a violent shaking for 30 seconds and allowed to stand. After five minutes the observations were made as to the amount of lather on the surface of each solution. Preliminary experiments showed that concordant results could not be obtained when the bottles were shaken in the two hands at the same time. Dilutions at each 100 cc. were tested both at 20° and 45° C.

Comparison of the depth of the layer of lather on the soap solutions with that on the soap solutions to which resene had been added showed a marked diminution due to the presence of resene at the following dilutions:

TABLE II  
Dilution showing decreased lather due resene

Soap	20°	45°
Laundry.....	400 cc.	600 cc.
Castile.....	800 cc.	1000 cc.
Toilet.....	1000 cc.	1200 cc.

From the figures in Table I it is seen that these differences in dilution correspond roughly to the percentages

<sup>1</sup> The analyses were made according to the method given in Lamborn's "Modern Soaps, Candles and Glycerine," p. 650.

of alkali salts of fatty acids in the respective soaps.

Another set of tests were made at 20° C., doubling the weight of resene added to the soap solution with the following results:

TABLE III

Soap	Dilution showing decreased lather due to resene
Laundry.....	400 cc.
Castile.....	600 cc.
Toilet.....	800 cc.

The identity of results in the case of the laundry soap is doubtless due to the crudity of the method of measuring the thickness of the lather layer. The decreased dilutions in the case of the castile and toilet soaps show again the injurious effect of resene on the lathering power of soap solutions.

A more marked evidence of the effect of added resene on the lather is shown by the time required for complete subsidence of the lather. These experiments were made at 20° C. Again, in each case, 5 cc. of the solutions used in Table II were diluted, shaken 30 seconds and allowed to stand until all lather had disappeared.

TABLE IV

DILUTION Cc.	Laundry		Castile		Toilet	
	S	S + R	S	S + R	S	S + R
100	24	6	72	36	168	120
200	6	1	50	30	168	36
300	4	0.66	48	24	72	24

The hours required for such subsidence are given in Table IV, in which S represents the standard soap solutions and S + R the solution of soap containing added resene.

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### PRELIMINARY NOTE ON DYES AND OTHER PRODUCTS FROM THE WASTE LIQUOR OF THE SODA CELLULOSE PROCESS

By MARSHALL P. CRAM  
Received August 20, 1914

If the crude black liquor obtained from the digesters in the soda process is treated with hydrochloric acid, a precipitate is formed which is wholly organic. The maximum yield of this precipitate is obtained when 100 cc. of the crude liquor of specific gravity 1.25 are treated with 30 cc. concentrated hydrochloric acid (sp. gr. 1.18), the yield from the 100 cc. crude liquor being 14 g. If the acidified solution is heated to boiling, the precipitate gathers in lumps which can be removed easily, the substance being plastic when hot and brittle when cold. It is soluble in alkalis and dilute alcohol. It is believed that the crude precipitate might be used for the following purposes.

I—SIZE FOR PAPER—The precipitate is soluble in dilute sodium hydroxide, 10 g. requiring about 470 cc. N/10 NaOH. For 10 g. dry pulp in 222 cc. water 0.22 g. of the precipitate dissolved in dilute NaOH, with an equal weight of aluminum sulfate added later, gave a paper which would be called hard-sized. This paper had a tint on the reddish brown, which could be increased by using more of the sizing substance. The color could not be removed by any method tried, but while this would prevent the use of the material for a size for white paper, it would not be objectionable for colored paper, and the color of the material

itself would be desirable for certain purposes. For 10 g. dry pulp, 0.054 g. of the material, followed by an equal weight of aluminum sulfate, gave a well sized paper, and 0.0135 g. a very light size. The crude liquor, which contains this precipitate already dissolved in NaOH together with inorganic salts, can also be used as a size for colored papers.

**II—STAIN AND VARNISH FOR WOOD**—The precipitate dissolved in dilute alkalis or alcohol can be applied to wood for a brown stain. It cannot be used as a varnish, for the residue contracts on drying. If, however, the total crude precipitate is treated with chloroform, about half the precipitate by weight dissolves; this solution on drying leaves a surface which does not contract, and which resembles varnish. It can be applied in chloroform, methyl or ethyl alcohol, or other volatile solvent. The part insoluble in chloroform can be used for a stain. There is some prospect that by precipitating the original precipitate fractionally, a fraction which can be used for a varnish might be obtained without using chloroform, but this has not been accomplished with entire success as yet.

**III—SULFUR DYE**—If the dry precipitate is mixed with powdered potassium sulfide (sodium sulfide has not been tried) and sulfur, and heated to 185° to 230° C., an odorless gas is given off, and the residue when extracted with water gives a solution which dyes wool, silk, and cotton a dark brown or black. The dye is taken by cotton without a mordant, and is quite fast to sunlight. Heating the mass to 310° destroys the dye which is first formed.

**IV**—If the precipitate is treated with nitric acid a solution is obtained which dyes wool brown if the acid is weak, or yellow if stronger acid is used. These dyes appear to be fast. They may also be obtained by nitrating the crude liquor.

If the filtrate from the precipitate thrown down with HCl is distilled, the distillate obtained contains acetic acid and some other compound, probably a phenol. Ten cc. of the distillate obtained from 150 cc. crude liquor with 45 cc. conc. HCl, when titrated with NaOH with phenolphthalein as indicator, required 40.3 cc. *N*/10 NaOH. The distillate with silver nitrate gave no precipitate of silver chloride, but on standing a red crystalline precipitate appeared. With a cold water solution of potassium nitrite the distillate gave a crystalline precipitate, the filtrate from which dyed wool and silk brown, but did not dye cotton. Crystalline precipitates were also obtained with nitric acid (this precipitate was dissolved if stronger nitric acid was added), ferric chloride, bromine water, and potassium permanganate. When treated with chlorine gas or a solution of bleaching powder the distillate gave a red solution which dyed wool and silk brown. The coloring matter could be removed from the water solution by extracting with chloroform.

The residue from the distillation could not be evaporated to dryness on the steam bath, which shows that some organic substance is present. The principal compound present, however, is sodium chloride,

from which the organic matter may be burned off. This residue left on evaporation if heated somewhat under certain conditions is partly changed to a substance soluble in dilute alcohol but not in water. The alcoholic solution on being evaporated leaves a varnish-like coating.

If the filtrate from the hydrochloric acid precipitate of the crude liquor, before being distilled, is extracted with chloroform and the chloroform evaporated, a red colored residue is left. This is somewhat soluble in hot water to a colloidal solution which dyes silk pink, but does not dye cotton or wool. The color on silk, however, fades very rapidly.

If this water solution is treated with bromine or chlorine, a solution is obtained which dyes wool brown and silk gray; these colors are much faster than the pink. Ammonium persulfate gives browns on silk and wool, but not on cotton. Potassium nitrite gives a brown for silk.

The reason for publishing this investigation in the above fragmentary form, is the hope that attention may be called by it to the possibilities of a present waste product and that investigation may be directed thereto, at this particularly opportune time.

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#### SOME RAPID METHODS FOR GLASS ANALYSIS<sup>1</sup>

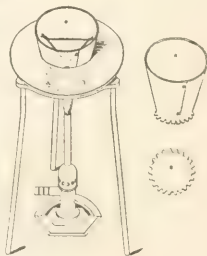
By E. C. SULLIVAN AND W. C. TAYLOR

Received August 15, 1914

Some convenient methods which we have developed for the routine analyses of glasses may be capable of further application and we therefore desire to bring them to the attention of others. Our original procedure for a complete analysis was to determine the alkalis by the J. Lawrence Smith method and the other bases and silica by fusion with soda. In some cases we were able to make use of the decomposition of glass by hydrofluoric and sulfuric acids. After some experimenting we found that we could use oxalic acid in place of sulfuric to decompose the fluorides. The oxalates can in turn be decomposed by heat so that no bases or acids are introduced to interfere with the determination of the glass constituents. By this method the complete analysis of a glass may be finished in one day.

This method was developed for the analysis of a large number of glasses of the same type. These contained silica, lead, soda and potash in varying proportions with small amounts of iron, alumina,

<sup>1</sup> The radiator used was made up from a description by W. F. Hillebrand in *Bulletin No. 422*, U. S. Geol. Survey, p. 31, and is described here as it has considerable influence on the success of the method. R is of sheet iron, aluminum or nickel. 6 to 7 cm. high, 8 cm. wide at top and 5 cm. at bottom. The base B may be of iron, nickel or platinum but not of aluminum, which will not stand the temperature of the direct flame. B is attached to R by turning the cogs of B up and over those of R. A platinum triangle should be inserted about 4 cm. from the base. An aluminum ring with an opening slightly larger than the underlying crucible should be placed over the radiator to hasten evaporation.





manganese, lime and magnesia as impurities. For these glasses the following method was used: One gram of finely powdered glass is placed in a platinum crucible of about 40 cc. capacity, moistened with water, 2 g. of  $\text{H}_2\text{C}_2\text{O}_4$  crystals added and enough 48 per cent HF to fill the crucible half full. This is evaporated to dryness on a radiator,<sup>1</sup> the temperature of which is just high enough to expel the excess of oxalic acid. When all the acid has been expelled the crucible is cooled and the evaporation repeated twice more with oxalic acid and water. The amount of oxalic acid used is about 5 g. in all. It was necessary to know the amount used as a blank showed 0.0012 g. of alkali chlorides from this source. After the third evaporation, when all the excess of oxalic acid is expelled, the remaining oxalates are taken up with hot water, allowed to cool and filtered. The residue which, in the case of the glasses mentioned, consists of  $\text{PbC}_2\text{O}_4$  only, with trace of  $\text{CaC}_2\text{O}_4$ , may be titrated directly with  $\text{KMnO}_4$  or dissolved in dilute  $\text{HNO}_3$  and determined as sulfate. The filtrate from the  $\text{PbC}_2\text{O}_4$  is evaporated to dryness in a platinum dish and then heated over a free flame until oxalates are decomposed. The carbonates are then taken up with water and HCl and the mixture is evaporated to dryness to remove the small amount of  $\text{SiO}_2$ . The salts are taken up with a few drops of HCl and hot water, a few drops of bromine water added, then a little ammonia, and the solution is boiled. The precipitate of hydroxides of iron, aluminum and manganese is filtered off, ignited and weighed. The filtrate is divided into two equal portions. To one are added  $\text{NH}_4\text{OH}$  and  $(\text{NH}_4)_2\text{HPO}_4$ , which precipitate a small amount of magnesia—about 1 mg. This is calculated to chloride and deducted from weight of NaCl, KCl. The other half is evaporated to dryness, ammonia salts expelled by heat and the chlorides weighed. The  $\text{MgCl}_2$  found and alkali from blank determination on all reagents are subtracted and the  $\text{K}_2\text{O}$  determined by the platinum chloride method and  $\text{Na}_2\text{O}$  by difference.

The following table will show some of the results obtained on weight of alkali chlorides from 1 g. sample:

Class No.	J. L. Smith method Gram	Oxalate Gram	Class No.	J. L. Smith method Gram	Oxalate Gram
1.....	0.170	0.175	2.....	0.177	0.189
	0.168	0.162	3.....	0.196	0.198
	0.176	0.169	4.....	0.1290	0.1294
		0.163	5.....	0.168	0.169

On the separation of soda and potash the oxalate method averages about 0.15 per cent lower in  $\text{K}_2\text{O}$  and correspondingly higher in  $\text{Na}_2\text{O}$ . The lead determination by the oxalate method expressed in per cent  $\text{PbO}$  compares as follows:

SODA FUSION	OXALATE
21.00	21.22
21.13	21.15
	21.30
	21.18

The combined weights of iron, alumina and manganese amount to from 1 to 1.5 per cent and average from 0.2 to 0.3 per cent lower by the oxalate method than by the soda fusion. The amounts of  $\text{CaO}$  and  $\text{MgO}$  are in the neighborhood of 0.1 per cent and are slightly lower by the oxalate method where determined though these determinations were usually omitted. We have

used this method since on a large number of similar samples and have found it satisfactory for glasses of this type.

In applying this method to other glasses the procedure following the three evaporations must of course be varied. The first step is to separate the soluble and insoluble oxalates. From there on the procedure may vary according to what elements are present. The oxalates we have worked with group themselves as follows:

INSOLUBLE				SOLUBLE		
Lead	Copper 2	Magnesium 2	Sodium	Potassium	Manganese 3	
Calcium	Cobalt 2				Iron 4	
Zinc	Nickel 2			Aluminum	Arsenic	
Cadmium 1	Barium 2			Chromium	Antimony 5	

1—Almost quantitative; in presence of zinc traces present with soluble oxalates.

2—Though mostly insoluble, these elements must be looked for with the soluble oxalates unless particular precautions are taken to have conditions right to render the oxalates insoluble. Presence of other elements also affects the solubility of these oxalates.

3—Manganese up to 2 per cent gave no test for the element with the insoluble oxalates but a glass containing 6 per cent  $\text{MnO}$  showed nearly half this amount as an insoluble oxalate.

4—Does not occur with insoluble oxalates except in zinc glasses when a small amount is found with the zinc.

5—Normally soluble but has been found with insoluble oxalates when these were heated too strongly.

Arsenic or antimony, if present, should be removed from the soluble oxalates with  $\text{H}_2\text{S}$  before the oxalates are decomposed. This necessitates acidifying with HCl, which must be expelled before decomposing the remaining oxalates; otherwise alkali chlorides are volatilized. The insoluble oxalates are in general dissolved in dilute HCl and separations made as in any mixture of chlorides. Borates do not interfere with the analysis. A number of analyses of glasses and silicates of other types are given to show results obtained by this method. The figures given are the difference between the oxalate method from the soda fusion and J. Lawrence Smith method. They are expressed as + when oxalate method is higher and — when lower.

	A	B	C	D	E	F
$\text{Na}_2\text{O}$ .....	-0.08	+0.36	-0.16	-0.11	+0.18	+0.14
$\text{K}_2\text{O}$ .....	-0.06	=0.00	+0.10	=0.00	-0.08	-0.04
$\text{CaO}$ .....	-0.22	-0.05		-0.05		
$\text{Al}_2\text{O}_3$ .....	+0.04	-0.08		=0.00	+0.03	-0.04
$\text{ZnO}$ .....		+0.13	+0.07	-0.30	+0.04	

A—An ordinary soda lime glass

B—A soda lime, zinc borosilicate

C—A soda potash zinc glass

D—A soda zinc borosilicate

E—A soda potash zinc glass

F—A soda alumina borosilicate

The presence of more than 3 per cent alumina causes difficulty, owing to its interfering with the expulsion of fluorine by oxalic acid. Except the lead glass all those containing  $\text{Al}_2\text{O}_3$  gave a test for fluorine in the soluble oxalates, and the amount of such fluorine was greater for high  $\text{Al}_2\text{O}_3$  content than for low.

Feldspar gave very low results for alkali. A sample yielding 0.1246 g. of alkali chlorides by the J. Lawrence Smith method gave 0.0909 g. by the oxalate method. This was increased to 0.1102 g. by reprecipitation of the alumina and to 0.1230 g. by a second reprecipitation. With several alumina glasses low results were obtained on both  $\text{Al}_2\text{O}_3$  and alkali, while with other glasses either  $\text{Al}_2\text{O}_3$  was low and alkali high or alkali was low and alumina high. From the data at hand it seems as if both alkali and  $\text{Al}_2\text{O}_3$  were apt to be lost at some stages of the analysis but so far our results are not consistent, probably due to the

variation in temperature in different analyses. In some we get conditions favorable for a loss of alkali, in some for a loss of  $\text{Al}_2\text{O}_3$  and sometimes for both. We have, with great care in heating, obtained only slightly low results where both  $\text{Al}_2\text{O}_3$  and  $\text{Na}_2\text{O}$  were very high as in cryolite. The loss therefore probably can be prevented.

Boric oxide tends to alleviate the difficulty caused by alumina and it does not in any way interfere with later determinations. Borosilicates with up to 5 per cent  $\text{Al}_2\text{O}_3$  give fairly good results. One showed 4.82 per cent  $\text{Al}_2\text{O}_3$  and 0.1010 g. alkali chlorides by regular methods and 4.93 per cent  $\text{Al}_2\text{O}_3$  and 0.1027 g. alkali chlorides by the oxalate method. The results on glass G mentioned in the table are not very good, however. With glasses not containing  $\text{B}_2\text{O}_3$  the addition of boric acid before evaporation with HF and  $\text{H}_2\text{C}_2\text{O}_4$  decreased the fluorine content of the soluble oxalates and also gave higher results for  $\text{Al}_2\text{O}_3$  and alkali without showing any  $\text{B}_2\text{O}_3$  present with the alkali.

From the results so far we do not feel confidence in the method for such glasses as show undecomposed silico-fluorides, for while accurate determinations may be obtained with special precautions the method has no advantages under such conditions. For glasses which do not contain much  $\text{Al}_2\text{O}_3$  the method seems well adapted, especially for the analysis of a series of glasses of very nearly the same composition. We have also found it convenient for the rapid determination of  $\text{As}_2\text{O}_3$  or  $\text{Sb}_2\text{O}_3$  in glass.

#### DETERMINATION OF BORIC ACID

In the analysis of borosilicate glasses we have found that for the determination of boric oxide the method described by Wherry<sup>1</sup> is very useful:

"Fuse the sample with about 3 g. of  $\text{Na}_2\text{CO}_3$  for 15 minutes. Take up with 20 to 30 cc. of dilute HCl adding a few drops of  $\text{HNO}_3$  to oxidize ferrous iron. Place in a 250 cc. round-bottomed flask, heat nearly to boiling, and add dry precipitated  $\text{CaCO}_3$  in moderate excess. Connect with a return condenser and boil vigorously for about 10 minutes. Filter out the precipitate through a small Büchner funnel, washing several times with hot water, but keeping the total volume of liquid below 100 cc. Return the filtrate to the flask, add a pinch of  $\text{CaCO}_3$  and again heat to boiling; then connect with a filter pump, through a splash trap, and continue suction until the boiling has nearly ceased. Cool to the ordinary temperature, filter if the precipitate has a red color from iron, add four or five drops of phenolphthalein and run in slowly  $N/10$  NaOH solution until the liquid is strongly pink in color. Introduce about 1 g. of mannite and shake, whereupon the pink color will disappear. Add NaOH to end reaction, then another gram of mannite and if necessary more alkali until a permanent pink color is obtained."

The method was first tried by fusing 0.5 g. sand and 0.2 g. boric acid with 3 g. soda. The melted mass was taken up with water and 7 cc. conc. HCl added after transfer to a 250 cc. flask. The method was then followed as described above except titration was made with  $\text{Ba}(\text{OH})_2$ . The  $\text{B}_2\text{O}_3$  content came from 2 to 10 per cent low, due to retention of  $\text{B}_2\text{O}_3$  by the precipitate from  $\text{CaCO}_3$ . By using suction in filtering and washing this precipitate practically 100 per cent of the  $\text{B}_2\text{O}_3$  introduced was recovered. For 0.25 g.  $\text{B}_2\text{O}_3 = 12.40$   $\text{Ba}(\text{OH})_2$  we used 12.35 and 12.40 cc.

<sup>1</sup> *J. Am. Chem. Soc.*, **30** (1908), 1687.

As iron and alumina are rarely present in large amounts in glass and as the time of the soda fusion with glass can be cut to a few minutes the method seemed quite readily adaptable.

The first glass tried was a soda alumina borosilicate which, from analysis, showed a possible  $\text{B}_2\text{O}_3$  content of 10.40 per cent by difference. Three determinations by Wherry's method showed 10.72, 10.57, 10.67 per cent  $\text{B}_2\text{O}_3$  or an average of 10.64 per cent. A soda borosilicate containing a small amount of BaO and  $\text{Sb}_2\text{O}_3$  showed 25.57 per cent  $\text{B}_2\text{O}_3$  by Wherry's method and 25.75 per cent by difference. Other glasses of same type showed:

Per cent $\text{B}_2\text{O}_3$ by titration	Per cent $\text{B}_2\text{O}_3$ by difference
25.10	25.12
12.71	12.15
17.57	17.51
14.90	15.01

With a zinc borosilicate very unsatisfactory results were obtained, the  $\text{B}_2\text{O}_3$  content by titration running from 4 to 9 per cent when only 2 per cent was present. Several mixtures of ZnO and sand with a known amount of  $\text{B}_2\text{O}_3$  were run through by Wherry's method and results for  $\text{B}_2\text{O}_3$  were always high even after very long boiling. Solutions of  $\text{ZnCl}_2$  and borax were boiled with  $\text{CaCO}_3$  for varying lengths of time and using slight excess and large excess of  $\text{CaCO}_3$  and zinc was always found in the filtrate from the  $\text{CaCO}_3$  precipitate. CaO was substituted for  $\text{CaCO}_3$  but with no better success.  $\text{Na}_2\text{CO}_3$  completely removed the zinc from solution and by a double precipitation, using first  $\text{Na}_2\text{CO}_3$  and then  $\text{CaCO}_3$ , we obtained 0.0360, 0.0361 and 0.0365 g.  $\text{B}_2\text{O}_3$  when the theoretical amount was 0.0365 g. PbO was found to cause the same trouble as ZnO and the same modification of the method gave satisfactory results. We have been able to use the modified method on a large number of glasses with satisfactory results.

The modified method then is as follows: Fuse 0.5 g. of glass with 3 g.  $\text{Na}_2\text{CO}_3$  for one or two minutes after mass is liquid. Take up with 20 to 30 cc. of hot water and when the melt is entirely decomposed filter out any insoluble oxides. After washing, transfer filtrate and washings to a 250 cc. round-bottomed flask, add about 7 cc. concentrated HCl, heat nearly to boiling and add dry precipitated  $\text{CaCO}_3$  in moderate excess. From here on the method is as given by Wherry except that we used  $\text{Ba}(\text{OH})_2$  instead of NaOH. It is also advisable to use suction for filtering the  $\text{CaCO}_3$  precipitate.

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#### THE COMPOSITION OF MILK AS SHOWN BY ANALYSES OF SAMPLES OF KNOWN PURITY MADE BY THE MASSACHUSETTS STATE BOARD OF HEALTH

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Milk, without doubt, is the most extensively adulterated of any article of human food and, by reason of its variable composition, the detection of this adulteration is difficult and in some cases impossible. For these reasons most legislative bodies, in addition to prohibiting the sale of adulterated milk, prohibit the sale of milk, the composition of which falls below

specified standards and in some places, as in the State of Massachusetts, the penalty for the sale of milk which is adulterated is more severe than that for the sale of milk below the legal standard. The milk analyst in such localities must familiarize himself with the composition of natural milk in order to detect and distinguish between milk which is adulterated and that which is simply below the legal standard. The usual methods of adulterating milk are the addition of water, the removal of cream or performance of both acts, the ease of which as well as the resulting profit has considerable to do with the extent of milk adulteration. As water is a natural component of milk, the detection of added water, as well as the removal of cream, can be accomplished only by showing abnormal chemical or physical constants which are consistent with the nature of the adulteration. Either or both of these forms of adulteration may be practised to a limited extent and be impossible of detection.

During the past six years, from 600 to 700 samples of known purity milk have been examined in the laboratory of food and drug inspection of the Massachusetts State Board of Health of which nearly 500 samples have been subject to a fairly complete analysis, 434 of which came from individual cows and the balance from herds. These samples were obtained from Jerseys, Guernsey, Ayrshire, Dutch Belt, and Holstein cows, as well as from cross-bred or so-called grade cows. The methods of analysis used were as follows:

**TOTAL SOLIDS,** as used by the Massachusetts State Board of Health for thirty years: Evaporate 5 g. of milk in a flat-bottomed platinum dish over a boiling water bath for 2 hrs. and weigh the residue.

**ASH:** Burn in a muffle the residue obtained as above, and weigh the ash.

**FAT:** By the Babcock method.

**PROTEINS:** From the percentage of nitrogen by the Gunning method using the factor 6.38.

**LACTOSE:** By the polariscopic method of the A. O. A. C., mercuric nitrate being used as a clarifier. If lead is used as a clarifier, the results are low, owing to the precipitation of lactose.

**MILK SERUM—(1) COPPER METHOD:**<sup>1</sup> Add four volumes of milk to one volume of copper sulfate solution (72.5 g. per liter adjusted to read 36.0 at 20° C. on the scale of the Zeiss Immersion Refractometer or to a specific gravity of 1.0443 at 20/4° C.), shake well and filter.

(2) **ACETIC ACID METHOD:**<sup>2</sup> To 100 cc. of milk add 2 cc. of 25 per cent acetic acid, heat for 20 minutes in a water bath at 70°, cool 10 minutes in ice water and filter.

(3) **MODIFICATION OF PFYL AND TURNAU**<sup>3</sup> called tetra serum I, giving the same serum which has been substituted in some instances for the acetic acid method. Shake 50 cc. of milk with 5 cc. of carbon tetrachloride in a shaking machine for 5 minutes, add 1 cc. of 20 per cent acetic acid, shake again for 5 minutes, centrifuge and pour off the clear serum.

(4) **SOUR SERUM:**<sup>1</sup> Allow the milk to sour spontaneously and filter.

(5) **ASH OF SOUR SERUM:**<sup>2</sup> Measure 25 cc. of the sour milk serum into a platinum dish, evaporate to dryness and burn in a muffle at a temperature not above 550° C. Weigh the residual ash.

The summary of the analyses of the samples arranged according to breeds in the order of the average total solids is given in Table I. Determinations of solids, fat, proteins, ash, and sugar were made upon all the samples, and the serum was prepared from nearly all the samples by one or more methods.

The variation in the composition of milk is due primarily to the breed of the cow but is more or less influenced by the period of lactation and the season of the year. It is very generally known that cows of the Jersey and Guernsey type give better milk than those of the Holstein variety, that cows far along in lactation give richer milk than just after calving and that milk obtained in the summer is inferior in quality to that obtained in the winter although popular opinion is opposed to this latter statement. The solids naturally show the highest numerical variation, from 17.17 to 10.20 per cent in the milk from individual cows and from 14.57 to 11.56 per cent in herd milk. The constituents having the most influence upon this variation are first the fat and to a less extent the proteins, the former varying from 7.7 to 2.45 per cent in milk from individual cows and from 5.40 to 3.35 per cent in herd milk and the latter from 5.01 to 2 per cent in milk from individual cows and from 4.02 to 2.66 per cent in herd milk. The numerical variation of the ash is very slight and that of the sugar is the least of the major constituents, the latter being from 5.80 to 3.91 per cent in milk from individual cows and from 5.25 to 4.35 per cent in herd milk.

The percentage variation is more marked than the numerical variation, being the greatest in the fat and least in the sugar. Owing to the presence of a few samples of abnormally high concentration, the percentage variations above the average are greater than those below the average.

Solids vary from 32 per cent above to 21 per cent below the average  
Fat varies from 83 per cent above to 42 per cent below the average  
Proteins vary from 53 per cent above to 39 per cent below the average  
Sugar varies from 32 per cent above to 18 per cent below the average  
Minimum solids were 40 per cent below the maximum solids  
Minimum fat was 68 per cent below the maximum fat  
Minimum proteins were 50 per cent below the maximum proteins  
Minimum sugar was 32 per cent below the maximum sugar

Excluding some of the abnormally high figures these variations would be reduced. It is unusual to find the solids above 17 or below 10.5 per cent, the fat above 7 or below 2.5 per cent, the proteins above 4.5 or below 2.4 per cent, the solids-not-fat above 10 or below 7.8 per cent, and the sugar above 5.5 or below 4.3 per cent. Using these limits, which eliminates 26 samples, the variations from the average are much less than those calculated from all the samples.

Solids would vary from 31 per cent above to 19 per cent below the average  
Fat would vary from 66 per cent above to 41 per cent below the average  
Proteins would vary from 38 per cent above to 27 per cent below the average  
Sugar would vary from 15 per cent above to 10 per cent below the average  
Minimum solids would be 38 per cent below the maximum solids  
Minimum fat would be 64 per cent below the maximum fat  
Minimum proteins would be 47 per cent below the maximum proteins  
Minimum sugar would be 22 per cent below the maximum sugar

<sup>1</sup> Matthes and Muller, *Z. Offenl. Chem.*, 9 (1903), 173.

<sup>2</sup> Burr and Berberich, *Chem. Ztg.*, 32, 617.

<sup>1</sup> Lythgoe, *Mass. State Board of Health Report*, 1908, p. 594.

<sup>2</sup> Leach and Lythgoe, *J. Am. Chem. Soc.*, 1904, p. 1195.

<sup>3</sup> *Arch. Kais. Ges.*, 40, 247.





The variations calculated from the analyses of the herd milk are, of course, much less than those obtained from the milk of individual cows. Experience has shown it to be improbable that cows giving abnormal milk will be present even in small herds of six or eight in sufficient numbers to render the herd milk abnormal. Of the herd milk,

Solids varied from 14 per cent above to 10 per cent below the average  
 Fat varied from 4 per cent above to 17 per cent below the average  
 Proteins varied from 21 per cent above to 20 per cent below the average  
 Sugar varied from 9 per cent above to 10 per cent below the average  
 Minimum solids were 21 per cent below the maximum  
 Minimum fat was 38 per cent below the maximum  
 Minimum proteins were 34 per cent below the maximum  
 Minimum sugar was 18 per cent below the maximum

The solids-not-fat (consisting of the proteins, lactose and ash) are much less variable than the solids or the fat and formerly was the only figure used in detecting added water, yet the variation here is considerable. A less variable figure, the soluble solids (consisting of the albumin, ash, and sugar varying between 5.95 and 6.45 per cent in herd milk and between 5.80 and 6.60 per cent in milk from individual cows), has been suggested by Cornalba<sup>1</sup> as a means of detecting added water, and this is substantially what is obtained when preparing the milk serum.

It has been known that the composition of milk is influenced by the season and by the time since calving. In order to show if these variations existed in the samples examined, the Grade Holstein, Grade Durham, Ayrshire and Grade Ayrshire milk were selected, thus excluding the exceptionally low Jersey and Guernsey and the exceptionally low Holstein and Dutch Belt figures. These 224 analyses were first arranged by months and because of the small number of samples obtained in some months, the averages were not representative and the arrangement was therefore made by seasons. Of these samples, the period of lactation was known in 194 cases and seasonal averages were made of these, together with averages of the same analyses arranged according to the period of lactation. These figures, together with the variation according to season of the herd milk, are shown in Table II.

TABLE II—KNOWN PURITY MILK SAMPLES ARRANGED ACCORDING TO SEASONS AND PERIOD OF LACTATION

HERDS	No. of samples	Total solids	Fat	Proteins	Ash	Solids not fat	Refraction of serum				Ash of sour serum	Protein-fat ratio	Per cent fat in solids	Average period of lactation
							Lactose	Copper	Acetic	Sour				
Winter (Dec.-Feb.)	9	13.23	4.20	3.41	0.76	9.03	4.88	37.9	44.3	42.2	0.779	0.81	31.7	
Spring (Mar.-May)	10	12.97	3.97	3.13	0.73	8.74	4.92	38.3	43.3	42.5	0.789	0.76	32.2	
Summer (June-Aug.)	8	12.39	3.73	3.15	0.75	8.66	4.71	37.5	42.3	42.2	0.853	0.84	30.1	
Fall (Sept.-Nov.)	13	12.85	3.94	3.37	0.74	8.91	4.80	37.7	42.8	41.7	0.775	0.86	30.7	
Average	45	12.79	4.03	3.31	0.74	8.76	4.83	37.8	42.7	42.3	0.792	0.82	31.6	
INDIVIDUAL COWS														
Winter (Dec.)	40	13.16	4.24	3.39	0.75	8.92	4.80	38.2	43.7	43.1	0.778	0.80	32.2	
Spring	88	12.72	4.00	3.16	0.75	8.72	4.78	37.7	42.5	42.0	0.811	0.79	31.4	
Summer	36	12.46	3.97	3.18	0.77	8.59	4.55	37.3	41.9	39.8	0.803	0.80	31.8	
Fall	60	12.79	3.97	3.28	0.73	8.82	4.84	37.9	42.4	40.4	0.801	0.83	31.1	
Average	224	12.76	4.03	3.23	0.74	8.73	4.77	37.7	42.5	41.3	0.809	0.80	31.6	
TIME SINCE CALVING														
1 month	25	12.70	3.98	2.93	0.73	8.72	4.90	38.1	42.1	42.6	0.785	0.74	31.3	3 weeks
2 to 5 months	82	12.76	3.97	3.19	0.74	8.79	4.86	37.7	42.6	41.8	0.779	0.78	31.1	3.4 months
6 to 9 months	58	13.03	4.14	3.43	0.75	8.89	4.71	37.7	42.3	42.0	0.817	0.83	31.7	7.5 months
10 to 15 months	29	13.15	4.22	3.43	0.76	8.93	4.75	37.7	43.4	42.2	0.788	0.81	32.1	10.6 months
Average	194	12.89	4.06	3.29	0.75	8.83	4.81	37.7	42.6	42.1	0.793	0.81	31.6	5.4 months
ABOVE SAMPLES ACCORDING TO SEASONS														
Winter	39	13.16	4.24	3.39	0.75	8.92	4.80	38.2	43.7	43.1	0.778	0.80	32.2	5.1 months
Spring	70	12.63	3.92	3.19	0.75	8.73	4.78	37.7	42.5	42.0	0.811	0.82	31.0	5.6 months
Summer	31	12.44	3.99	3.18	0.75	8.45	4.55	37.3	41.9	39.8	0.803	0.80	32.0	5.6 months
Fall	34	12.84	4.00	3.27	0.76	8.84	4.87	37.9	42.4	40.4	0.801	0.82	31.2	4.7 months

A perusal of this table concerning the seasonal variation shows that milk obtained in the winter is the best, that obtained in the summer is the worst, while milk obtained in the spring and fall is a mean of the summer and winter samples. These differences, however, are

by no means as marked as those observed between the different breeds. The period of lactation appears to have no influence upon the variation by season for in the series of 194 samples arranged by seasons, the average period of lactation was practically the same in each season. All the results are affected by the seasonal variation and all but the sugar and serum figures are affected by the period of lactation. The protein-fat ratio and the percentage of fat in the solids of these samples were not materially affected either by the season or by the period of lactation.

#### RELATION BETWEEN THE MILK SOLIDS AND ITS CONSTITUENTS

**RELATION BETWEEN THE SOLIDS AND THE FAT**—The percentage of fat in the solids decreases with the solids; in the Jersey milk, it averages 38 and in the Holstein milk 27 per cent. The highest figure was 47.4 obtained from a sample of Jersey milk and the lowest 25.0 per cent, from a sample of Holstein milk.

**RELATION BETWEEN THE SOLIDS AND PROTEINS**—The amount of proteins in the solids is fairly constant at about 25 per cent. Olson<sup>1</sup> has given for the approximate calculation of the protein from the solids the formula  $P = TS \frac{TS}{1.34}$  where P equals proteins and T S equals total solids.

**RELATION BETWEEN THE SOLIDS AND THE ASH**—As the ash is nearly constant, the percentage of ash in the solids increases as the solids diminish, being 4.9 in Jersey milk and 6.7 per cent in Holstein milk.

**RELATION BETWEEN THE TOTAL SOLIDS AND SUGAR**—Like the ash the sugar is nearly constant and the percentage of sugar in the solids increases as the solids decrease. In Jersey milk the average figure is 30 and in Holstein milk 40 per cent.

#### RELATION BETWEEN THE DIFFERENT MILK CONSTITUENTS

**PROTEIN-FAT RATIO**—This has been extremely studied

by Van Slyke<sup>2</sup> and his average ratios being based upon several thousand analyses are of more value than those shown in Table I. The figures for the protein-fat ratio for the different breeds are as follows:

<sup>1</sup> Ann. Fals., 1, 256.

<sup>2</sup> J. Am. Chem. Soc., 30, 1166.

Breed	Protein-fat ratio	From Table I	Breed	Protein-fat ratio	From Table I
Holstein-Friesian	1 : 0.87	1 : 0.86	Shorthorn	1 : 0.80	
Dutch Belt		1 : 0.83	Devon	1 : 0.80	
Ayrshire	1 : 0.82	1 : 0.75	Guernsey	1 : 0.66	1 : 0.71
American Hollderness	1 : 0.83		Jersey	1 : 0.64	1 : 0.61

There seem to be three groups of cows according to the protein-fat ratio, those of the Jersey type with the protein-fat ratio below 0.7, those of the Holstein type with the protein-fat ratio above 0.85, and the balance of the breeds with a protein-fat ratio about 0.8. Van Slyke has given for the approximate calculation of the proteins from the fat, the formula  $P = 0.4(F - 3) + 2.8$  where P equals proteins and F equals the fat.

TABLE III. CALCULATED SUGAR

FAT	10.5	10.6	10.7	10.8	10.9	11.0	11.1	11.2	11.3	11.4	11.5	11.6	11.7	11.8	11.9	12.0	12.1	12.2	12.3	12.4	12.5	12.6	12.7	12.8	12.9	13.0	13.1	13.2	13.3	13.4	13.5	13.6
%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
25	4.63	4.70	4.78	4.86	4.93	5.01	5.08	5.15	5.23	5.31	5.38	5.46	5.53	5.60	5.68	5.76	5.83	5.90	5.98	6.05	6.13	6.20	6.28	6.35	6.43	6.50	6.58	6.66	6.73	6.80	6.88	6.96
26	4.70	4.80	4.90	5.00	5.10	5.20	5.30	5.40	5.50	5.60	5.70	5.80	5.90	6.00	6.10	6.20	6.30	6.40	6.50	6.60	6.70	6.80	6.90	7.00	7.10	7.20	7.30	7.40	7.50	7.60	7.70	7.80
27	4.78	4.88	4.98	5.08	5.18	5.28	5.38	5.48	5.58	5.68	5.78	5.88	5.98	6.08	6.18	6.28	6.38	6.48	6.58	6.68	6.78	6.88	6.98	7.08	7.18	7.28	7.38	7.48	7.58	7.68	7.78	7.88
28	4.86	4.96	5.06	5.16	5.26	5.36	5.46	5.56	5.66	5.76	5.86	5.96	6.06	6.16	6.26	6.36	6.46	6.56	6.66	6.76	6.86	6.96	7.06	7.16	7.26	7.36	7.46	7.56	7.66	7.76	7.86	7.96
29	4.93	5.03	5.13	5.23	5.33	5.43	5.53	5.63	5.73	5.83	5.93	6.03	6.13	6.23	6.33	6.43	6.53	6.63	6.73	6.83	6.93	7.03	7.13	7.23	7.33	7.43	7.53	7.63	7.73	7.83	7.93	8.03
30	5.01	5.11	5.21	5.31	5.41	5.51	5.61	5.71	5.81	5.91	6.01	6.11	6.21	6.31	6.41	6.51	6.61	6.71	6.81	6.91	7.01	7.11	7.21	7.31	7.41	7.51	7.61	7.71	7.81	7.91	8.01	8.11
31	5.08	5.18	5.28	5.38	5.48	5.58	5.68	5.78	5.88	5.98	6.08	6.18	6.28	6.38	6.48	6.58	6.68	6.78	6.88	6.98	7.08	7.18	7.28	7.38	7.48	7.58	7.68	7.78	7.88	7.98	8.08	8.18
32	5.15	5.25	5.35	5.45	5.55	5.65	5.75	5.85	5.95	6.05	6.15	6.25	6.35	6.45	6.55	6.65	6.75	6.85	6.95	7.05	7.15	7.25	7.35	7.45	7.55	7.65	7.75	7.85	7.95	8.05	8.15	8.25
33	5.23	5.33	5.43	5.53	5.63	5.73	5.83	5.93	6.03	6.13	6.23	6.33	6.43	6.53	6.63	6.73	6.83	6.93	7.03	7.13	7.23	7.33	7.43	7.53	7.63	7.73	7.83	7.93	8.03	8.13	8.23	8.33
34	5.31	5.41	5.51	5.61	5.71	5.81	5.91	6.01	6.11	6.21	6.31	6.41	6.51	6.61	6.71	6.81	6.91	7.01	7.11	7.21	7.31	7.41	7.51	7.61	7.71	7.81	7.91	8.01	8.11	8.21	8.31	8.41
35	5.38	5.48	5.58	5.68	5.78	5.88	5.98	6.08	6.18	6.28	6.38	6.48	6.58	6.68	6.78	6.88	6.98	7.08	7.18	7.28	7.38	7.48	7.58	7.68	7.78	7.88	7.98	8.08	8.18	8.28	8.38	8.48
36	5.46	5.56	5.66	5.76	5.86	5.96	6.06	6.16	6.26	6.36	6.46	6.56	6.66	6.76	6.86	6.96	7.06	7.16	7.26	7.36	7.46	7.56	7.66	7.76	7.86	7.96	8.06	8.16	8.26	8.36	8.46	8.56
37	5.53	5.63	5.73	5.83	5.93	6.03	6.13	6.23	6.33	6.43	6.53	6.63	6.73	6.83	6.93	7.03	7.13	7.23	7.33	7.43	7.53	7.63	7.73	7.83	7.93	8.03	8.13	8.23	8.33	8.43	8.53	8.63
38	5.61	5.71	5.81	5.91	6.01	6.11	6.21	6.31	6.41	6.51	6.61	6.71	6.81	6.91	7.01	7.11	7.21	7.31	7.41	7.51	7.61	7.71	7.81	7.91	8.01	8.11	8.21	8.31	8.41	8.51	8.61	8.71
39	5.68	5.78	5.88	5.98	6.08	6.18	6.28	6.38	6.48	6.58	6.68	6.78	6.88	6.98	7.08	7.18	7.28	7.38	7.48	7.58	7.68	7.78	7.88	7.98	8.08	8.18	8.28	8.38	8.48	8.58	8.68	8.78
40	5.76	5.86	5.96	6.06	6.16	6.26	6.36	6.46	6.56	6.66	6.76	6.86	6.96	7.06	7.16	7.26	7.36	7.46	7.56	7.66	7.76	7.86	7.96	8.06	8.16	8.26	8.36	8.46	8.56	8.66	8.76	8.86
41	5.83	5.93	6.03	6.13	6.23	6.33	6.43	6.53	6.63	6.73	6.83	6.93	7.03	7.13	7.23	7.33	7.43	7.53	7.63	7.73	7.83	7.93	8.03	8.13	8.23	8.33	8.43	8.53	8.63	8.73	8.83	8.93
42	5.91	6.01	6.11	6.21	6.31	6.41	6.51	6.61	6.71	6.81	6.91	7.01	7.11	7.21	7.31	7.41	7.51	7.61	7.71	7.81	7.91	8.01	8.11	8.21	8.31	8.41	8.51	8.61	8.71	8.81	8.91	9.01
43	5.98	6.08	6.18	6.28	6.38	6.48	6.58	6.68	6.78	6.88	6.98	7.08	7.18	7.28	7.38	7.48	7.58	7.68	7.78	7.88	7.98	8.08	8.18	8.28	8.38	8.48	8.58	8.68	8.78	8.88	8.98	9.08
44	6.06	6.16	6.26	6.36	6.46	6.56	6.66	6.76	6.86	6.96	7.06	7.16	7.26	7.36	7.46	7.56	7.66	7.76	7.86	7.96	8.06	8.16	8.26	8.36	8.46	8.56	8.66	8.76	8.86	8.96	9.06	9.16
45	6.13	6.23	6.33	6.43	6.53	6.63	6.73	6.83	6.93	7.03	7.13	7.23	7.33	7.43	7.53	7.63	7.73	7.83	7.93	8.03	8.13	8.23	8.33	8.43	8.53	8.63	8.73	8.83	8.93	9.03	9.13	9.23
46	6.21	6.31	6.41	6.51	6.61	6.71	6.81	6.91	7.01	7.11	7.21	7.31	7.41	7.51	7.61	7.71	7.81	7.91	8.01	8.11	8.21	8.31	8.41	8.51	8.61	8.71	8.81	8.91	9.01	9.11	9.21	9.31
47	6.28	6.38	6.48	6.58	6.68	6.78	6.88	6.98	7.08	7.18	7.28	7.38	7.48	7.58	7.68	7.78	7.88	7.98	8.08	8.18	8.28	8.38	8.48	8.58	8.68	8.78	8.88	8.98	9.08	9.18	9.28	9.38
48	6.36	6.46	6.56	6.66	6.76	6.86	6.96	7.06	7.16	7.26	7.36	7.46	7.56	7.66	7.76	7.86	7.96	8.06	8.16	8.26	8.36	8.46	8.56	8.66	8.76	8.86	8.96	9.06	9.16	9.26	9.36	9.46
49	6.43	6.53	6.63	6.73	6.83	6.93	7.03	7.13	7.23	7.33	7.43	7.53	7.63	7.73	7.83	7.93	8.03	8.13	8.23	8.33	8.43	8.53	8.63	8.73	8.83	8.93	9.03	9.13	9.23	9.33	9.43	9.53
50	6.51	6.61	6.71	6.81	6.91	7.01	7.11	7.21	7.31	7.41	7.51	7.61	7.71	7.81	7.91	8.01	8.11	8.21	8.31	8.41	8.51	8.61	8.71	8.81	8.91	9.01	9.11	9.21	9.31	9.41	9.51	9.61

Shortly after the Olson formula was published, it occurred to the writer that since Olson's formula and that of Van Slyke were correct only when applied to pure milk, a combination of both formulas might be used in distinguishing between pure and adulterated milk. The sugar was chosen as the possible index and calculations were made upon many samples of milk, using the following formulas:

$$I. S = T - [F + 0.7 + (T - \frac{T}{1.34})]$$

$$II. S = T - [F + 0.7 + (0.4(F - 3)) + 2.8]$$

where S equals the milk sugar, T S the total solids, F the fat, and 0.7 the ash.

It was found that the values of S obtained by both formulas were nearly the same when the milk was pure and varied from 4.5 to 5 per cent. In skimmed or watered samples, the values disagreed and were above 5 in the former and below 4 per cent in the latter. A table was then prepared, using the above formulas for milk with solids from 10.5 to 12.5 per cent and fat from 2.5 to 4 per cent. This table has been in constant use for 5 years for the purpose of distinguishing between skimmed milk, whole milk and watered milk. From

an extension of this table a list of the maximum and minimum fat corresponding to the total solids from 10.5 to 4 per cent was prepared and published in the 1909 report of the Massachusetts State Board of Health. Subsequent experience, however, has shown that for practical purposes, the maximum and minimum values could be placed farther apart. In Table III of calculated sugar, the upper values for the sugar were obtained by Formula I, the lower values by Formula II. The positions of the heavy lines were determined by allowing the variations of not more than



one-tenth in the calculated sugar values. The samples falling above the other heavy lines may be suspected of being skimmed, those falling below the lower line may be watered, and those falling between these lines are probably normal milk. If a sample is both skimmed and watered, it may be classed in this table as normal milk, but usually, when both such acts are performed, either one or the other preponderates to such an extent that the sample will appear adulterated.

Five hundred and seventy-four samples of milk of known purity and 2168 commercial samples which could not be declared adulterated with a variation in solids from 11 to 13.6 per cent have been tabulated with reference to the relation between the solids and the fat and the results of this tabulation are shown

sample is either watered or skimmed as the case may be. Considerable more work must be done, however, involving the tabulation of several thousand analyses of samples of known purity milk from individual cows in order to establish the accuracy of the above statement.

**MILK SERUM**—Milk serum has been extensively used for the detection of added water in milk<sup>1</sup> and its value for this purpose is due to the fact that in the preparation of serum the most variable components of the milk, the fat and casein, have been removed. Of the various methods for the preparation of the serum, the writer prefers the copper method on account of the simplicity and rapidity of its preparation, because it can be prepared without heat and requires but a small quantity of milk. With the small beakers now in use with the

TABLE IV  
RELATION BETWEEN THE TOTAL SOLIDS AND FAT OF 2168 SAMPLES OF MILK WHICH WERE NOT DECLARED ADULTERATED

FAT PER CENT	TOTAL SOLIDS PER CENT																										NO. OF SAMPLES			
	11.0	11.1	11.2	11.3	11.4	11.5	11.6	11.7	11.8	11.9	12.0	12.1	12.2	12.3	12.4	12.5	12.6	12.7	12.8	12.9	13.0	13.1	13.2	13.3	13.4	13.5		13.6		
	NUMBER OF SAMPLES																													
2.5	1																											1		
2.6																												1		
2.7																												2		
2.8																												7		
2.9	1	1	1	1	1	2		2	3	2		1																15		
3.0	2		3	3	5	3	1	3	3		2	1																26		
3.1			2	2	4	3	3	2	4	4	4	6	4	4														42		
3.2	1	1		3	1	7	6	8	7	5	7	11	15	3		2	2	4			1							86		
3.3			2		2	5	5	16	14	14	12	6	8	7	6	6	5	4					1					113		
3.4					2	4	1	3	4	5	7	9	14	13	14	13	12	8	6	6	4	1						131		
3.5						2	4	1	1	6	7	13	13	20	23	21	12	18	6	2	4	3	2		1			159		
3.6				1	2	3		2	3	2	8	15	15	23	40	28	21	13	9	8	5	5	2	3		1		209		
3.7					2					4	1	6	5	8	11	14	30	22	32	35	32	26	10	4	2	2	3	1	250	
3.8							1			1	1	1	3	4	13	19	20	37	29	42	32	32	12	4	5			258		
3.9												2	2	8	7	13	14	19	25	27	23	27	18	16	10	1	3	2	217	
4.0												2		5	4		1	20	25	27	23	19	21	22	20	10	8	5	3	215
4.1																3	4	3	10	8	17	16	26	12	21	10	8	3	142	
4.2																2	2	3	2	7	3	9	8	16	13	17	12	10	104	
4.3																1	1		2	2	1	3	8	7	7	14	8		60	
4.4																					2	6	1	8	3	15	13	8	37	
4.5																		1			1	1	2	6	5	8	6		30	
4.6																							3	3	2	4	6	5	23	
4.7																									3	1		5	10	
4.8																											5	1	7	
4.9																											1		3	
NO. OF SAMPLES	5	2	9	13	26	31	21	43	48	48	66	80	108	112	153	143	173	163	157	140	138	111	95	87	70	77	49	2168		

in Tables IV and V. In both of these tables the zone of pure milk is indicated as in Table III. It appears from these tables that the methods in use for the detection of added water are efficient but that those for the detection of skimming are not so reliable. A larger percentage of known milk purity fell below the lower heavy line than of the commercial samples not declared adulterated. The samples above the upper heavy line which may be suspected of being skimmed, constituted 17 per cent of the known purity samples and 47 per cent of the commercial samples. Of the samples containing less than 3.3 per cent of fat, 5 per cent of the known purity samples and 68 per cent of the commercial samples were above the upper heavy line. Table III is intended solely for the purpose of selecting the particular samples which are to be subjected to other tests for adulteration and to give a positive indication of the character and possible extension of the adulteration. From Table V it would seem that if a sample was 0.4 above or 0.4 below the maximum or minimum fat figure corresponding to the solids the

Zeiss immersion refractometer, it is possible to obtain sufficient filtrate from a 10 cc. sample and if one is in a hurry 17.6 cc. of milk will give sufficient filtrate in a few minutes. This method has been criticized by the author<sup>2</sup> and subsequently by Ackermann<sup>3</sup> on account of the dilution necessary in the preparation of the serum, but this is offset by less variation in the serum from different samples. It has another disadvantage, that it is not possible to use the values of the ash of the copper serum in detecting added water because the amount of copper in the serum is higher in watered milk than in unwatered milk and consequently the ash in the serum of watered samples is but little less than in the serum of the original milk before watering. This objection is also applicable to the calcium chloride serum of Ackerman, owing to the precipitation of the calcium phosphate in the preparation of the serum.<sup>4</sup>

<sup>1</sup> For an extensive and complete review of the literature on this subject, see *Arch. Kois. Gesundheits.*, 40, Heft. 3.

<sup>2</sup> Eighth Intern. Congr. of Appl. Chem., 1, p. 308.

<sup>3</sup> *Z. Nahr. Genussm.*, 24 (1912), 612.

<sup>4</sup> *Arch. Kois. Gesundheits.*, 40, pp. 248, 255 and 256.

The acetic method as modified by Pfyl and Turnau is fairly rapid when only a few samples are examined. It can be prepared at the room temperature, the dilution is but 2 per cent and the ash figures increased by 2.21 per cent, are comparable with those obtained

hibits signs of becoming sour, the only serum that should be prepared is the spontaneously obtained sour serum.

RELATION BETWEEN THE CONSTITUENTS OF MILK SERUM—Milk serum consists of water, sugar, lactic

TABLE V  
RELATION BETWEEN THE TOTAL SOLIDS AND FAT OF 574 SAMPLES OF MILK OF KNOWN PURITY

FAT PER CENT	TOTAL SOLIDS PER CENT																																		NO. OF SAMPLES
	11.0	11.1	11.2	11.3	11.4	11.5	11.6	11.7	11.8	11.9	12.0	12.1	12.2	12.3	12.4	12.5	12.6	12.7	12.8	12.9	13.0	13.1	13.2	13.3	13.4	13.5	13.6	NUMBER OF SAMPLES							
2.5																																			
2.6																																			
2.7																																			
2.8																																	3		
2.9																																	5		
3.0																																	13		
3.1																																	13		
3.2																																	28		
3.3																																	43		
3.4																																	41		
3.5																																	42		
3.6																																	43		
3.7																																	47		
3.8																																	34		
3.9																																	40		
4.0																																	44		
4.1																																	30		
4.2																																	33		
4.3																																	33		
4.4																																	24		
4.5																																	22		
4.6																																	12		
4.7																																	11		
4.8																																	5		
4.9																																	1		
NO. OF SAMPLES	9	5	16	19	16	13	17	23	27	12	33	28	32	24	21	30	28	20	32	22	22	23	25	25	22	16	14					574			

from the sour serum. The greatest value of the sour serum is in the preparation of the ash. Using 25 cc. of sour milk serum there is less than 2 g. of organic matter to be burned and the influence of the combustion of this upon the 100 milligrams of ash is slight. It is advisable to apply this test in addition to the refraction or specific gravity of the serum to all samples suspected of containing added water, for both figures depend upon different milk constituents and, furthermore, if milk is declared adulterated by both methods, it eliminates the possibility of the samples being naturally abnormal milk obtained from a sick cow. It will be noticed in Table I that the refraction of the sour serum is midway between that of the copper serum and the acetic serum. This should be borne in mind when making examinations of milk which have par-

acid, more or less protein, and mineral matter, depending upon the mode of preparation. The acetic serum contains sugar, coagulable albumen, protein precipitated by tannic acid and all the mineral matter. The sour serum contains the same substances in addition to lactic acid formed from the sugar. The copper serum contains the sugar, coagulable albumen, protein precipitated by tannic acid, and some of the mineral matter. The calcium chloride serum contains the sugar, proteins precipitated by tannic acid, and a portion of the mineral matter, but no coagulable albumin.

The refractive index of milk serum is an additive property consisting of the sum of the refractive indices of its constituents, and except in the case of the calcium chloride serum, bears no absolute relation to the com-

TABLE VI—RELATION BETWEEN SERUM REFRACTION AND SOUR SERUM ASH  
Refraction of copper serum

Ash of sour serum	36	37 38 39 40 Per cent of samples				Totals	38 39 40 41 42 43 44 45 Per cent of samples									Totals
	0.7 0.730 0.750 0.770 0.790 0.810 0.830 0.850 0.870 0.890 0.910	1.4 2.1 1.4 2.8 1.4 0.7 0.7 0.7 0.7	7.8 6.4 6.4 5.6 2.1 0.7 0.7 0.7 0.7	2.1 3.5 3.5 3.5 2.1 0.7 0.7 0.7 0.7	0.7 0.7 0.7 0.7 0.7 0.7 0.7 0.7 0.7		12.7 18.3 22.7 21.1 11.2 5.6 4.2 2.1 2.1	0.8 0.8 0.7 0.7 0.7 0.8 0.8 0.8 0.8	2.3 2.3 2.3 2.3 2.3 0.7 0.8 0.7 0.8	0.8 3.1 3.8 3.8 1.5 1.5 1.5 0.8 0.8	3.1 4.6 6.2 6.1 3.9 4.6 3.9 1.5 1.5	2.3 2.3 2.3 2.3 2.3 0.8 0.8 0.8 0.8	2.3 4.6 0.8 0.8 1.5 0.8 0.8 0.8 0.8	13.9 16.9 23.1 21.5 10.7 4.6 4.6 3.1 1.6		
TOTALS	11.9	25.4	44.4	16.9	1.4	100.0	2.3	5.4	12.3	13.7	27.0	24.6	10.0	4.7	100.0	

tially soured. Under such circumstances, the copper serum so prepared will give a higher reading and the acetic serum a lower reading than would be given by the same sample before souring. When a sample ex-

position of the milk from which it was made. In the calcium chloride serum, the refractive indices follow very closely the percentage of sugar in the milk. There is no specific relation between the ash of the

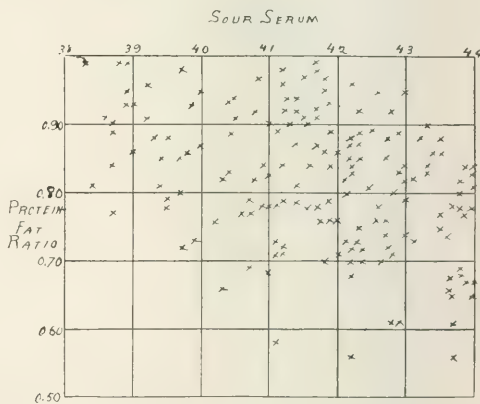
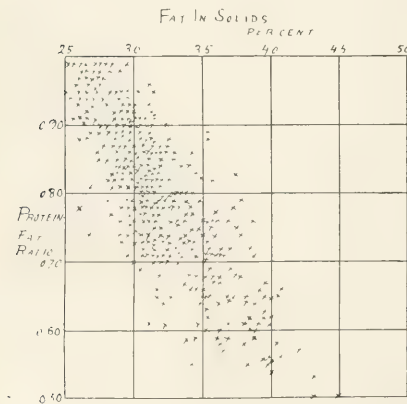
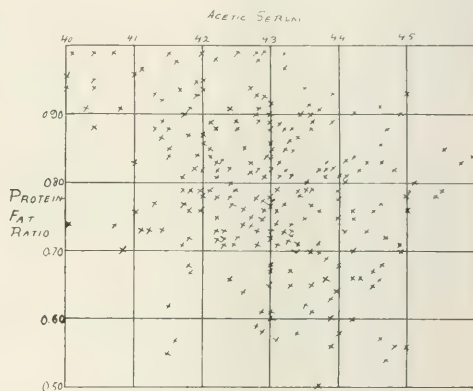
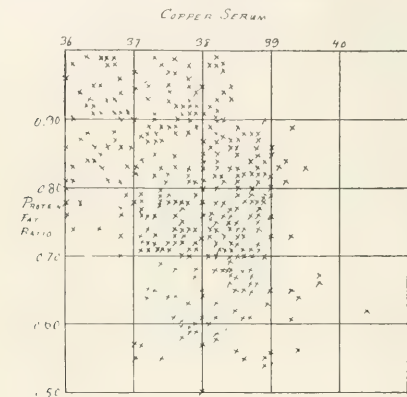
sour serum and the other properties of the serum of pure milk, as shown in Table VI, computed from the refractions of copper serums of 142 samples, the refraction of the sour serum of 130 samples, and the ash of the sour serums of the same samples.

It is possible, however, if one knows the refractive indices of the milk serum to calculate with accuracy the specific gravity or the solids of the same serum.

The Lorenz and Lorentz formula  $\frac{n^2 - 1}{n^2 + 2} \cdot d = K$  where

no difference in the value of  $K$ , provided that the refractive index and specific gravity are determined at the same temperature and the latter referred to water at 4° C. Where the values of  $n$  and  $d$  are obtained at different temperatures, the value of  $K$  varies with the temperature. In the formula  $\frac{n^2}{n^1} = A$ ,  $n$  and  $n^1$

must be determined at the same temperature. The value of  $K$  in the copper serum is slightly less in watered milk than in whole milk, due to the fact that while



$n$  equals the refractive index,  $d$  the specific gravity, and  $K$  a constant, is uniform for various concentrations of milk serum and may be used to calculate the specific gravity from the refractive index. The formula evolved by Walter and Robertson<sup>1</sup>  $\frac{n^2}{n^1} = A$  where

$n$  equals the refractive index of the solution,  $n^1$  the refractive index of the solvent,  $c$  the concentration of the solution, and  $A$  a constant, is applicable for the calculation of solids of the milk serum. The values of these constants are given below. In the Lorenz and Lorentz formula, the difference in temperature makes

the refraction of the copper solution is about the same as that of the milk serum, its specific gravity is higher. The variation, however, is too slight to have any marked effect upon the calculation of the specific gravity from the refractions. Table VIII gives the value of the specific gravity and solids calculated from the refraction figures of the acetic and copper serums and of the specific gravity calculated from the sour serum.

RELATION OF THE PROTEIN-FAT RATIO TO SERUM REFRACTION—It will be seen from Table I that in the samples obtained from Jersey and Guernsey cows, no figures for copper refraction were obtained below 37.0 and the figures for the protein-fat ratio were all less

<sup>1</sup> Wied. Ann., 38 (1889), 107; J. Phys. Chem., 13 (1909), 469



TABLE VII—RELATION BETWEEN SERUM CONSTANTS

Serum	$n_D^{20} - 1$	$d$	$K$	$n_D^{20} - 1$	$A$
Calcium chloride	$n_D^{20} + \frac{1}{2} \cdot \frac{d}{K}$	at 17.6° C.	$K = 0.2056$ (a)		
	$d$ at 15/15° C.				
Acetic	$n_D^{20} + \frac{1}{2} \cdot \frac{d}{K}$	at 17.6° C.	$K = 0.2054$ (b)	$A = 0.00158$ (b)	
	$d$ at 15° C.				
Copper	$n_D^{20} + \frac{1}{2} \cdot \frac{d}{K}$	at 17.6° C.	$K = 0.20592$ (b)		
	$d$ at 15° C.				
Sour	$n_D^{20} + \frac{1}{2} \cdot \frac{d}{K}$	at 17.6° C.	$K = 0.20526$ (b)	$A = 0.00158$ (b)	
	$d$ at 15° C.				
	$n_D^{20} + \frac{1}{2} \cdot \frac{d}{K}$	at 15° C.	$K = 0.20581$		
	$d$ at 15° C.				
	$n_D^{20} + \frac{1}{2} \cdot \frac{d}{K}$	at 15°/4° C.	$K = 0.20607$ (b)		

(a) Weigner and Yakuwa, *Milchweiser. Zentr.*, 6 (1909), 473.(b) Lythgoe, *Proc. Eighth Intern. Congr. Appl. Chem.*, 1, 309

than 0.82 and from the average figures it appears that as the protein-fat ratio increases, the concentration of the serum diminishes. All the refraction figures corresponding to protein-fat ratio above 0.50 have been

TABLE VIII—COMPARISON BETWEEN REFRACTIVE INDICES AND OTHER CONSTANTS OF MILK SERUM (CALCULATED FROM FORMULAS GIVEN IN TABLE VII)

Scale reading	$n_D^{20}$	ACETIC SERUM Solids Per cent	SP. GR. 15°/15° 20°/4°	COPPER SERUM Solids Per cent	SP. GR. 15°/15° 20°/4°	SOUR SERUM Solids Per cent	SP. GR. 15°/15° 20°/4°
20° C.	20° C.						
28.0	1.33820	3.30	1.0149	1.0131	3.30	1.0184	1.0163
29.0	1.33861	3.35	1.0160	1.0141	3.35	1.0194	1.0173
30.0	1.33896	3.78	1.0170	1.0151	3.78	1.0203	1.0184
31.0	1.33934	4.02	1.0180	1.0161	4.02	1.0215	1.0194
32.0	1.33972	4.26	1.0190	1.0172	4.26	1.0225	1.0204
33.0	1.34010	4.51	1.0200	1.0181	4.51	1.0235	1.0214
34.0	1.34048	4.74	1.0211	1.0193	4.74	1.0246	1.0225
35.0	1.34086	4.98	1.0221	1.0203	4.98	1.0256	1.0235
36.0	1.34124	5.22	1.0231	1.0213	5.22	1.0267	1.0246
37.0	1.34162	5.46	1.0242	1.0223	5.46	1.0277	1.0256
38.0	1.34199	5.70	1.0252	1.0233	5.70	1.0288	1.0266
39.0	1.34237	5.94	1.0262	1.0243	5.94	1.0298	1.0276
40.0	1.34275	6.18	1.0273	1.0254	6.18	1.0308	1.0287
41.0	1.34313	6.42	1.0283	1.0264	6.42	1.0318	1.0297
42.0	1.34350	6.66	1.0293	1.0274	6.66	1.0328	1.0307
43.0	1.34388	6.90	1.0303	1.0284	6.90	1.0338	1.0317
44.0	1.34426	7.14	1.0313	1.0295	7.14	1.0348	1.0327
45.0	1.34463	7.38	1.0323	1.0305	7.38	1.0358	1.0337

plotted and the results are shown in the chart on page 906. From this chart, it is apparent that normal milk with a protein-fat ratio less than 0.70, should give sera with refractive indices above 37 by the copper serum, 40 by the sour method, and 41 by the acetic method. The relation between the protein-fat ratio and the percentage of fat in the solids is shown in the plot. The protein-fat ratio increases as the percentage of fat in the solids decreases; therefore, if the per cent of fat in the solids is high (above 35), the sample should give a serum with a high refraction. The consideration

TABLE IX—ANALYSES OF HERD MILK OF KNOWN PURITY

No.	Total solids Per cent	Fat Per cent	Protein Per cent	Solids-not-fat Per cent	Lactose Per cent	Fat in solids Per cent	Refraction of serum 20° C.	Sour serum ash G. per 100 cc.
1	14.18	4.70	3.46	0.73	9.48	5.03	7.4	33.2
2	13.96	4.70	3.25	0.78	9.26	5.16	6.99	33.6
3	13.34	4.30	3.20	0.70	9.64	5.05	6.74	32.2
4	13.10	4.20	3.22	0.73	8.90	5.12	6.72	32.1
5	12.97	4.40	3.07	0.76	8.57	4.80	6.70	33.9
6	12.85	4.10	3.17	0.66	8.75	5.04	6.77	31.9
7	12.80	3.85	3.35	0.74	8.95	4.85	6.87	30.1
8	12.76	4.10	2.98	0.76	8.66	4.60	6.73	32.1
9	12.58	3.60	3.38	0.74	8.98	4.64	6.94	28.6
10	12.44	3.70	2.98	0.66	8.74	4.93	6.81	29.8
11	12.30	3.80	3.01	0.72	8.50	4.96	6.79	30.8
12	12.26	3.70	3.22	0.74	8.46	5.12	6.72	32.1
13	12.19	3.65	2.94	0.70	8.54	4.63	6.81	29.9
14	12.14	3.40	3.15	0.75	8.74	4.70	6.93	28.0
15	11.74	3.30	2.96	0.78	8.44	4.59	6.80	28.1
16	11.28	3.20	2.83	0.74	8.08	4.35	6.89	28.5

of these relations should be studied in connection with the other figures obtained from the same sample, particularly with the sour serum ash, before the sample is called watered.

During the months of March, April and May of this

year, the milk of a large number of herds has been examined in connection with another investigation. From these, sixteen have been chosen, including the samples from which the highest and lowest figures have been obtained; the analyses are recorded in Table IX. The character of the herds, the number of cows and the amount of milk obtained at the milking, is given in Table X. None of these analyses were used in the preparation of Table I.

Sample No. 12 was obtained from a celebrated herd of thoroughbred Holstein Fresian cows, the majority of which were in the last stages of lactation. Sample

TABLE X—CHARACTER OF HERDS PRODUCING THE MILK RECORDED IN TABLE IX

No	Jersey	Grade			Grade Holstein	Holstein	Total no cows	Wt. of milk	
		Guernsey	Guernsey	Durham				Ayrshire	Lbs
Number of cows									
1	20						20		
2		35		2		2	39	450	11.6
3	4	4				5	13		
4	2	4			8	8	22	250	11.7
5	2	5	8			12	27	329	12.2
6	4				8	14	30	400	13.3
7	1	1		4			29	240	12.6
8			4	10	3	4	3	25	260
9	4		4			20	28	273	9.7
10			2			13	15	180	12.9
11							39	500	12.0
12							25	217	8.7
13			9	1			36	46	580
14						10	10		
15						24	24	325	13.5
16						12	12	167	14.3

No. 15 was obtained from the same herd two months later, many of the cows having freshened since the previous sample was taken. The analyses of these two samples show that while the solids and the fat were both much lower in the second sample taken, there was practically no difference between the figures obtained from the milk serum.

All the other samples were taken from different herds. The milks from herds Nos. 14, 15 and 16 are not sold at retail until after being mixed with milk of good quality, in order to bring it up to the requirements of the Massachusetts law.

## SUMMARY

Variations in the composition of milk are due primarily to the breed, and to a less extent to the season of the year and to the time since calving.

The least variable milk constituents are the lactose and ash, both of which are of value in detecting added water.

It is possible, within reasonable limits, to indicate from the percentage of solids and fat, whether or not a sample has been watered, skimmed, or is normal milk.

No relation exists between the refraction of the serum and the sour serum ash; therefore, if both figures are below the minimum for pure milk it is positive indication of the presence of added water.

The protein fat ratios in all cases have been less than 1. If this figure exceeds 1, skimming is indicated, the amount being greatest in samples possessing the highest ratio.

If the protein-fat ratio is less than 0.7 or the percentage of fat in the solids is above 35.0, samples may be declared watered by a low refraction of the serum, not

necessarily below the minimum for all samples of known purity. This is particularly so when dealing with herd milk.

In the absence of a refractometer, the specific gravity or the per cent of solids of the serum is just as valuable as the refractive index in detecting added water.

The writer wishes to acknowledge his thanks to his assistants, Messrs. Charles H. Hickey, Louis I. Nurenberg, and Clarence E. Marsh, to whom he is greatly indebted for their valuable coöperation in making the analyses of the samples.

LABORATORY OF FOOD AND DRUG INSPECTION  
MASSACHUSETTS STATE BOARD OF HEALTH  
BOSTON

### SOME CHARACTERISTICS OF CHLORINE-BLEACHED FLOUR

By C. A. A. UTT

Received July 3, 1914

Since the Government ruled against flour treated with the oxides of nitrogen (F. I. D. 100; N. T. 722, U. S. Dept. of Agr.), chlorine-bleached flour has made its appearance. United States Patent 1,071,977, September 29, 1913, deals with a process in which "flour is treated with anhydrous chlorine (diluted with an inactive gas) in order to mature and whiten it." This process and a few others in which chlorine is the active agent are used. By this means, it is claimed, the flour is whitened and aged.

That chlorine will bleach flour has been known for many years, but its activity and difficulty of control have caused its use to be viewed with suspicion. In connection with the pure food work of Kansas it was found necessary to collect some information on chlorine-treated flour. The results of this investigation are presented in this paper.

Samples were obtained directly from the mills by the Kansas food inspectors, of the same flour before and after bleaching. These were placed in screw-top glass jars, sealed and shipped to the laboratory. The following determinations were made: (1) Chlorine qualitatively and quantitatively; (2) moisture; (3) acidity. A number of gluten and baking tests were also made.

Chlorine was determined by Jacobs' method as used in the Plant Chemistry Laboratory of the U. S. Department of Agriculture. It is as follows: "To 25 grams of flour in a platinum dish, add 25 cc. of a solution containing 25 grams of KOH and 25 grams  $\text{KNO}_3$  per liter. Evaporate to dryness on a steam bath, and ignite in a muffle at a dull red heat until thoroughly charred. Extract the charred mass with 25 cc. 5 per cent  $\text{HNO}_3$ ; filter. Return residue to the platinum dish, char further and extract again with 25 cc. 5 per cent  $\text{HNO}_3$ ; filter, wash with hot water, and ignite to an ash. Dissolve the ash in 5 per cent  $\text{HNO}_3$ , filter and wash. Combine the filtrates and determine the chlorine with silver nitrate."

Qualitative determinations of chlorine were made by the copper wire method as given by Alway (*Bull. 102*, Nebraska Experiment Station, page 53) as follows: "One ounce (30 grams) of flour is extracted with benzene

(ether was used) and the latter evaporated. A small amount of oil remains. A piece of copper wire is heated in a colorless gas flame until it is black and no longer colors the flame green. The hot end of the wire is dipped into the oil and again brought into the flame. If chlorine or bromine has been used as a bleaching agent a green or blue coloration is produced."

Moisture determinations were made by drying the samples for five hours in a steam oven at the temperature of boiling water.

The determinations of acidity were made in accordance with Method 5 in *Bull. 152*, of the Bureau of Chemistry, U. S. Department of Agriculture, which is as follows: To 20 grams of flour in a 500 cc. Erlenmeyer flask add 200 cc. freshly boiled water. Digest at 40° C. for two hours, shaking at 10-minute intervals. Decant the clear liquid through a folded filter and titrate 50 cc.  $N/20$  NaOH.

Table I indicates the results obtained on inspection samples. It will be noted that the moisture does not vary any more between the bleached and unbleached flour than might be expected in duplicate determinations. An increase in acidity in the bleached

TABLE I—SOME CHARACTERISTICS OF CHLORINE-BLEACHED FLOUR

NO.	Description	Moisture	Acidity, as lactic acid	Cl p m Copper wire reaction	Vol. of loaf	Gluten		Grade of loaf	
						Moist	Dry	Color	Texture
46-47	Unbleached patent	13.36	0.126	484 +	1870	43.1	12.99	94	95
	Bleached patent	13.68	0.144	764 +	1860	42.8	13.07	93	94
48-45	Unbleached, clear	14.72	0.198	532 +	1780	47.5	16.10	..	83
	Bleached, clear	14.18	0.288	916 +	1800	48.6	16.07	..	85
52-54	Patent unbleached	10.70	0.162	442 +	1940	38.7	12.67	93	92
	Patent bleached	11.12	0.18	881 +	1950	39.16	12.87	93	89
65-66	Unbleached patent	12.66	0.176	556 +	2020	39.34	12.40	94	92
	Bleached patent	12.88	0.126	648 +	1980	39.98	12.92	93	89
95-96	Unbleached	12.20	0.144	494 +	1920	41.83	14.05	94	94
	Bleached	12.24	0.189	716 +	1970	41.78	13.67	93	94
91-92	Patent unbleached	13.10	0.126	540 +					
	Patent bleached	13.12	0.135	844 +					
51-55	Unbleached, clear	12.44	0.216	504 +					
	Bleached, clear	12.32	0.252	928 +					
97-98	Unbleached	11.46	0.189	544 +					
	Bleached	11.40	0.198	868 +					
70299	Bleached	10.99	0.198	736 +					
70300	Bleached	11.22	0.207	900 +					
65-63	Unbleached	12.88	0.306	576 +					
	Bleached	12.69	0.324	667 +					
70-72	Unbleached	12.56	0.18	501 +					
	Bleached	12.68	0.234	972 +					
73-71	Unbleached	12.42	0.216	496 +					
	Bleached	12.42	0.270	855 +					

flour as compared with the corresponding unbleached sample is noted in nearly every instance. The chlorine content varies from 442 parts per million to 576 parts per million in the unbleached flour; when bleached the variation is 648 to 972 parts per million. All bleached samples reacted positively with the copper wire reaction for chlorine.

The differences in loaf volume are not much greater than one would expect to find in individual loaves from the same flour. Loaf volume favors the unbleached flour in some cases, in others the bleached flour. All loaves were graded against a standard loaf made from hard wheat flour under the same conditions, as is the custom. It will be noted that in nearly every case the bread made from the unbleached flour grades better. The bleached flour gives a loaf having an objectionable color and texture.

The gluten tests run practically uniform for the bleached and unbleached flour, there being no more difference than on duplicates. However, physically

the gluten of the chlorine-treated flour is somewhat softer in some cases, showing that the chlorine may have affected the gluten to some extent.

Several samples of unbleached flour gave the following amounts of chlorine, expressed in parts per million: (1) 445; (2) 503.8; (3) 492; (4) 448; (5) 348; (6) 373; (7) 452; (8) 484; (9) 496; (10) 544. A number of samples of chlorine-treated flour on the Kansas market yielded the following amounts of chlorine expressed in parts per million: (1) 742; (2) 260; (3) 591; (4) 608; (5) 732; (6) 712; (7) 1056; (8) 904. All of these gave a positive test with the copper wire reaction.

A number of samples of bleached and unbleached flour were shipped to the laboratory in cloth sacks, packed together. The unbleached flour yielded the following amounts of chlorine, parts per million: (1) 528; (2) 552; (3) 612; (4) 598; (5) 592. In each case a slight color developed in the copper wire reaction, showing that some chlorine was probably taken up by the unbleached flour. A sample of soft wheat gave 452 parts chlorine per million; a sample of hard wheat gave 496 parts, and two samples of bran gave 464 and 431 parts chlorine per million.

#### SUMMARY

The chlorine content of untreated flour may run as high as 576 parts per million. Chlorine-treated flour will contain over 600 parts per million of chlorine.

The chlorine can be detected with certainty by means of the copper wire reaction. Samples of unbleached flour in contact with chlorine-treated flour may give the reaction.

Chlorine-treatment increases the acidity of the flour and does not improve its breadmaking qualities.

In conclusion credit should be given to Miss Leila Dunton of the Department of Milling Industry of the Kansas State Agricultural College for making the baking and gluten tests, and to Dr. J. T. Willard, of the Department of Chemistry, for suggestions in carrying out the work.

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#### DETERMINATION OF PRUSSIAN BLUE IN TEA<sup>1</sup>

By G. W. KNIGHT

Received August 31, 1914

This method of determining the artificial coloring matter, Prussian blue, on tea is the conclusion of a series of experiments to ascertain an analytical method that would be rapid, accurate and quantitative. By means of it, 1 part in 200,000, and sometimes even 1 part in 300,000, can be detected. A man inexperienced in the manipulation can run four determinations in a day easily, and doubtless with experience could run many more. Two operators working independently on the same sample obtained 0.0019 and 0.0016 per cent of Prussian blue.

**METHOD**—100 g. of tea are ground to a fine powder in a coffee grinder, placed in a round-bottomed distilling flask of sufficient capacity and moistened with enough 85 per cent phosphoric acid to thoroughly

<sup>1</sup> Contributed with the permission of the Secretary of the Treasury and the U. S. Appraiser, Port of New York.

moisten all of the tea. (Usually from 30 cc. to 60 cc. are sufficient.) The flask is then fitted with a delivery tube, which passes through a two-hole stopper into a mixture of 4 cc. of 10 per cent NaOH solution and 30 to 40 cc. of water contained in a 100 cc. Erlenmeyer flask. The Erlenmeyer flask is supported in a beaker of cold water.

An outlet tube bent at right angles passes through the other hole of the two-hole stopper for the escape of unabsorbed gases. The apparatus is placed in a well ventilated hood and a Bunsen burner flame is placed in front of the outlet tube to burn the unabsorbed gases.

The flask is then heated, slowly at first, with a small flame and finally more strongly until the phosphoric acid begins to distil over. Usually 10 or 15 minutes are sufficient for the distillation.

After the distillation is completed, the distillate is filtered and the filtrate placed in a casserole; if acid, it is neutralized with 10 per cent NaOH solution, then 3 cc. of 10 per cent NaOH solution in excess are added. A crystal of  $\text{FeSO}_4$  about the size of a pea and a few drops of 10 per cent  $\text{FeCl}_3$  solution are added and the solution boiled for 1 minute. HCl (sp. gr. 1.2) is then added, drop by drop, to the hot solution till it is distinctly acid. The solution is filtered and the precipitate washed with 95 per cent alcohol, until the washings run colorless. Cold 10 per cent NaOH solution is dropped on the filter, using as little as possible but washing the whole area of the filter, and then the filter is washed with as small an amount of water as possible. It is best to drop the wash water, drop by drop, from a pipette. About 4 cc. of NaOH and 8 cc. of water are sufficient for this operation.

The filtrate is acidified with acetic acid and a few drops of HCl (sp. gr. 1.2), a few drops of 10 per cent  $\text{FeCl}_3$  solution are added and then HCl (sp. gr. 1.2) is added until any brown color that may have developed has disappeared.

The solution is then placed in a casserole and evaporated to half its bulk on the water bath; more water is added to dissolve any salts that may have crystallized out, and the Prussian blue is filtered on a Gooch crucible, washed with very dilute HCl, water, alcohol and ether, and dried at 100° C. to constant weight.

The weight in grams gives directly the per cent of Prussian blue in the sample.

Several samples of uncolored China and Japan teas were run by this method, and no Prussian blue detected. Then varying amounts of Prussian blue, from 1 part in 75,000 to 1 part in 400,000, were mixed with these uncolored teas. Prussian blue was obtained in all cases up to 1 part in 200,000 and in some cases up to 1 part in 300,000. The amount appeared proportionate to that put in, but the amount was too small to weigh except in the case of 1 part in 75,000; and in this case where 1.5 mg. was put in 1 mg. was recovered. As the purity of the Prussian blue put in was questionable, this was a fairly quantitative recovery.

Three samples which gave 1 spot, 2 spots and 3



spots, respectively, by the Read test,<sup>1</sup> gave 0.0005, 0.0022 and 0.0022 per cent, or 1 part in 200,000, 1 part in 45,000, and 1 part in 45,000.

Three other samples of colored tea that gave an average of 50 spots, 48 spots and 32 spots, respectively, by the Read test, and showed color distinctly in 1 and 2 and barely perceptibly in 3 by a qualitative infusion method devised by W. G. Berry (unpublished) gave 0.0072, 0.0044 and 0.0016 per cent, or 1 part in 14,000, 1 part in 23,000, and 1 part in 63,000. Sample number 3 repeated by a different operator gave 0.0019, checking fairly well with 0.0016 by the first operator.

The writer contemplates making a more exhaustive study of the method as to its suitability in the analysis of various classes of tea.

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### AN INVESTIGATION OF THE DIASTASE OF ALFALFA AND THE EFFECT OF RAPID CURING UPON THE FOOD VALUE OF ALFALFA<sup>2</sup>

By RALPH C. SHUEY  
Received May 22, 1914

#### INTRODUCTION

In a search for a commercial source of diastase among the green plants, alfalfa was found to have an exceptionally high diastatic content, and further work indicated a close relation between diastatic content and the proportion of water-soluble constituents of the dried plant. It was found possible, by careful and rapid curing, to increase the diastatic value very materially; and this paper will deal principally with these relations and their possible economic importance. Before taking up the experimental work, however, it might be well to review briefly the occurrence of diastase, its role in the economy of the green plant and the chemical changes related thereto.

Diastase, or amylase, may be defined as that enzyme or organic catalyst which is elaborated by the living organism for the purpose of assisting in or bringing about the conversion of starch into sugar. But little is known of the chemical nature of diastase. As ordinarily prepared, the substance contains nitrogen and might be classed with the proteins, but some work of Frankel and Hambourg<sup>3</sup> and others indicates that the protein may not be necessarily an integral part of the substance, but that the protein and diastase are almost inseparable on account of their colloidal nature and other physical properties. The action of diastase is easily affected by slight variations in conditions. Aside from the temperature and concentrations of hydrolyte, hydrolyst and hydrolytic products, the presence of very slight amounts of hydrogen—or hydroxyl-ions or of salts may produce very great changes in the activity or even completely inhibit action. In the moist state or in solution, diastase is easily destroyed by heat, continued heating at 80° C.,

being sufficient but if perfectly dry a temperature of 100° C. for a considerable time has no noticeable effect.

As we are not concerned with the diastases of animal origin, they will not be discussed. The vegetable sources of diastase may be roughly divided into three groups:

I—In the green plants diastase is present for the conversion of the deposited storage material, starch, into the soluble and transportable sugars which may, after transportation, be again deposited as one of the less soluble carbohydrates, starch or cellulose, or may be used up in the metabolic processes of the plant. The diastase from green plants possesses the property of dissolving unboiled or granular starch to a much greater degree than does that from the other two sources.

II—The germinating seeds elaborate a very active diastase for the purpose of making available to the growing embryo the stored up material of the endosperm. Although this diastase attacks unboiled starch, it does so only very slowly. Malted or sprouted grain is the most generally known source of diastase. Aside from its use in the fermentation industries as malt, the soluble portions, concentrated to a syrup or powder, are used in the baking industry and in medicine.

III—Many of the fungi and bacteria secrete diastase for the purpose of making available the food material of a starchy medium in which they are growing. This has found application in the moyashi or yeast used in making the Japanese alcoholic drink, *sake*, from rice. The diastatic extract from this fungus, *Aspergillus oryzae*, is used in medicine under the name Taka-diastase.

#### HISTORY: THE PRESENCE OF DIASTASE IN GREEN PLANTS

The first investigation of diastatic activity in green plants noted was that of Kosmann<sup>1</sup> in 1877. He made aqueous infusions of lichens, moss, algae and fungi, precipitated with alcohol, and obtained a substance which showed diastatic action in every case when starch paste was used as hydrolyte, and even in some cases when unaltered starch was used.

The following year a monograph was published by Baranetsky,<sup>2</sup> describing similar work on the seeds, bulbs, stems and leaves of plants. His conclusions were that the quantity of enzyme present at any one time was very small, it being elaborated as needed and used up as fast as formed.

J. Boehm<sup>3</sup> agreed with the former investigators and added this piece of information, that freezing and thawing the leaves stops the depletion of starch, as does also immersion in an atmosphere of hydrogen. None of these investigators used any antiseptic precautions and their tests were more qualitative than quantitative.

In 1884, Brasse<sup>4</sup> followed Kosman and Baranetsky but used chloroform as an antiseptic and measured the diastatic activity by means of the quantitative reduction of copper solutions in place of using the iodine

<sup>1</sup> "Eighth International Congress of Applied Chemistry," Vol. XVIII. p. 301.

<sup>2</sup> This investigation was made in connection with Industrial Fellowship No. 2, in the University of Kansas, during the years 1907-10, and has been withheld from publication in fulfillment of the conditions of the Fellowship Agreement.

<sup>3</sup> *Woch. fur Braue.*, 23 (1906), 473.

<sup>1</sup> *Bull. Soc. Chim.*, 27 (1877), 251.

<sup>2</sup> "Die Starkeumbildenden Fermente in den Pflanzen," Leipzig, 1878.

<sup>3</sup> *Zeit. fur d. g. Braue.*, 6 (1883), 76.

<sup>4</sup> *Comptes Rendus*, 99 (1884), 878.

test for starch. He found diastase in the precipitate formed by adding strong alcohol to solutions of potato, dahlia, Jerusalem artichoke, corn, beet, tobacco and ricinus leaves.

Schimper<sup>1</sup> found feeble diastatic action in all leaves he investigated and noted that *Allium cepa* did not form starch within its chlorophyll granules. He thought that perhaps this might be due to a high diastatic activity in the leaf preventing the formation of solid starch. However, comparisons of *Allium* with *Euphorbia* and *Tropaeolum*, which form starch abundantly, showed the latter to possess much higher diastatic activity, leading to the conclusion that the diastase bears a direct relation to the starch present.

Then Wortman<sup>2</sup> raised a dissenting voice. Using the clear filtrate obtained by shredding and pounding leaves with water, he found no diastatic action in 27 out of the 32 species examined and only very feeble action in the other 5. Both 0.5 per cent starch solution and unaltered wheat starch were used as hydrolyte. Leaves kept in an atmosphere of CO<sub>2</sub> in the dark did not lose starch, while those kept in oxygen lost starch readily. From these results he concluded that the role of diastase in the plant was either very unimportant or that it had no function whatever and that the solution of the starch was brought about by the direct action of the living protoplasm. He admitted one exception, that of germinating seeds.

S. H. Vines<sup>3</sup> almost immediately published a criticism of Wortmann's work, objecting to the iodine starch determination in the presence of leaf extract, for Wortmann himself had shown that coloring matter and foreign substances interfered with the color reaction. In his own work he found the turbid extract much more active than the clear filtrate. In some cases the added starch solution hindered the hydrolysis of the starch naturally occurring in the plant. He concluded that the carbohydrate formed was not maltose. Vines' work agreed with that of Baranetsky and Boehm and he concluded that, although the amount of diastase that could be extracted was small, yet the secretion was doubtless a continuous process, so that the amount produced during a given time might suffice to effect the observed conversion of starch into sugar.

A. Prunet<sup>4</sup> observed that the end sprouts of a sprouting potato developed much faster than those near the middle and examination showed much more diastase in the ends of the potato, thus showing a relation between the production of diastase and the dissolution of starch. He also found a relation between the appearance of diastase and the commencement of growth in the tubers.

A. Meyer<sup>5</sup> studied and tabulated the starch-forming ability of the leaves of different plants and found that many of the monocotyledons do not store starch. He concluded, however, that this was not due to the rapid removal of carbohydrates. He arranged the plants

into five orders of decreasing starch storage, placing the Solanaceae and Papillonaceae first. He also found that leaves could convert sugars into starch when the plucked leaves were immersed in sugar solution.

Brown and Morris<sup>1</sup> in 1893 published an extensive research into the diastase of leaves. After determining the diastase in the leaves of many different species, they concluded that it was always present in quantities sufficient to hydrolyze more starch than the leaf could contain at any one time, sometimes enough to hydrolyze many times the dry weight of the leaf itself. Tannin very often prevented the making of an extract of any power, although by precipitating the tannin with rawhide raspings the diastase could be demonstrated. They concluded that neither the leaf nor the powdered tissue gave a full measure of the diastase present, for drying and powdering the leaf and using a suspension of the powder in water gave an activity about seven times greater than the filtered extract of the crushed green leaf. The Papillonaceae and Solanaceae proved to be exceptionally high in diastase. Expressing the diastatic activity by the number of grams of maltose produced in 48 hours' hydrolysis at 30° by ten grams of dry leaf, they found in *Pisum sativum* an activity of 240.3°, about one-third the activity of pale barley malt.

The diastase was found to be from 35 per cent to 70 per cent more active in leaves plucked after being kept in the dark some hours than after a full day's insolation. In one case keeping in the dark for four days increased the activity 153 per cent, but this was with a very feebly diastatic sample. Although floating leaves on water in the dark increased the diastase just as keeping the growing plant in the dark had done, yet floating on a dilute solution of dextrose in the dark decreased the diastatic activity. From this and the results of similar experiments<sup>2</sup> on sprouting grains they concluded the secretion of diastase to be a starvation phenomenon.

Leaf diastase was found capable of acting on solid starch, especially that of buckwheat. In the presence of 0.006 per cent formic acid a suspension of *Pisum sativum* caused complete disintegration of many of the soaked buckwheat starch grains placed in it for 10 hours at 30° C. When acting on boiled starch the resulting carbohydrates were found to be maltose and dextrin, but no dextrose.

After studying the relation of leaf starch to the total products of assimilation, they concluded that "There is no evidence whatsoever of starch being a necessary link between the sugars of assimilation and the sugars of translocation; it is far more probable that the starch is only elaborated within the cell when the supply of nutrient is in excess of the cell requirements and that most of the assimilated products never pass through the stage of starch at all." They found sucrose to be the prevailing sugar in the juice of the plants examined.

Browne and Blouin<sup>3</sup> found in the sugar cane leaves

<sup>1</sup> Bot. Zeit., 43, 1885, p. 738.

<sup>2</sup> Ibid., 1890, p. 582.

<sup>3</sup> Ann. of Bot., 5 (1891), 409.

<sup>4</sup> Comptes Rendus, 115 (1892), 751.

<sup>5</sup> Bot. Zeit., 1888, pp. 27-32.

<sup>1</sup> Jour. Chem. Soc. Trans., 63 (1893), 604.

<sup>2</sup> Brown and Morris, Jour. Chem. Soc. Trans., 57 (1890), 458.

<sup>3</sup> La Agr. Exp. Sta., Bull. 91.

a much higher percentage of sucrose in the evening than in the morning. The carbohydrates were transported as reducing sugars which were reconverted to sucrose and stored up in the pith cells. A portion of the invert sugar was used up in the vital processes of the cane (formation of new tissue, etc.) for which purpose levulose appeared to be used in greater amount.

Butkewitsch<sup>1</sup> found a very active diastase in the bark of a number of plants and stated that in the barks of some of the Papillonaceae it is only slightly inferior to malt in its activity.

The presence of diastase in the leaves, stalks, bark and ripening fruit<sup>2</sup> makes it appear that diastase is present in all parts of plants, at least at some period during their growth.

The success of these investigations, demonstrating the presence of such appreciable quantities of diastase, indicated the probability of the diastatic content of fodders bearing an important relation to the availability of the food constituents. Experiments were conducted along similar lines, using alfalfa as an example of a highly diastatic plant, and endeavoring to learn the optimum conditions for the production and retention of diastase in a cured hay.

#### METHODS AND PROCEDURE

**PREPARATION OF SAMPLES**—All samples of alfalfa, except when otherwise noted, were cut when from  $\frac{1}{10}$  to  $\frac{3}{10}$  in bloom, the stems from the different plants thoroughly mixed and afterwards divided into 1000 or 2000 gram portions for curing. The control samples were placed in ovens immediately and dried at 45–50° C. for 48 hours. The "air cured" samples were allowed to lie on the floor of the laboratory for three days and afterwards dried at 45–50° C. for 48 hours to bring them to the same moisture content as the controls. All samples, after the treatment noted, received this final drying.

In the sampling of the stacks several samples were taken from different parts of the stack by raising a portion of the hay on poles and removing an armful from the undisturbed portion, being careful not to shake off any leaves. These samples were mixed, coarsely ground and resampled for final grinding.

If leaves and stems were determined separately, after drying, the leaves were stripped from the stems by hand, weighed and ground separately. This method of separation, although extremely crude, gave a maximum error of about 2 per cent.

**DIASTASE DETERMINATION**—Starch paste—2000 grams of distilled water were roughly weighed into a tared beaker and boiled. Forty grams of neutral soluble starch prepared according to Lintner<sup>3</sup> were accurately weighed out and stirred with about 100 cc. of water and added to the bulk of the water with stirring and the whole boiled and stirred for five minutes, then cooled and made up to exactly 2000 grams.

Two and one-half grams of the dry pulverized plant were accurately weighed into a 100 cc. wide-mouthed bottle and exactly 50 cc. of water added from a pipette. Two drops of toluene were added and the whole allowed

to digest for eight hours at room temperature with occasional shaking. This was filtered through an empty porcelain Gooch crucible until clear, the pulverized plant acting as filtering medium. This gave about 45 cc. of liquid which was assumed to contain  $\frac{45}{1000}$ ths of the water-soluble substance of the plant. Experiment showed this assumption to be within experimental error.

For digestion 100 cc. portions of the starch solution were measured into 120 cc. tubes, placed in a water bath at 40°, and allowed to come to that temperature: 5 cc. of plant solution were added to a tube of starch solution which was then stoppered and well shaken and 25 cc. immediately withdrawn and placed in a 200 cc. Erlenmeyer flask containing 5 drops of alkaline Fehling solution. This sample was used for the purpose of determining the amount of sugar present before digestion and the alkaline solution was used merely to stop further action and so allow the solution to stand until cupric reduction could be determined. The time required for filling the tubes was noted and at the end of exactly one hour 25 cc. portions were withdrawn into flasks as before, so gauging the time that both the first and last tubes had exactly one hour for digestion.

Ten cc. each of Allihn's modification of Fehling's solution<sup>1</sup> and 25 cc. of water were measured into an Erlenmeyer flask and heated to boiling. This solution was added to one of the digestion samples, the whole heated to boiling and allowed to boil for exactly four minutes. The mixture was filtered immediately through a Gooch filter containing a good thick mat of asbestos. After thoroughly washing, the filter, tube and stopper were transferred to a 250 cc. flask and 4 cc. of concentrated nitric acid were added to the precipitate: 1 cc. of acid was also added to the precipitating flask to dissolve any adhering copper oxide and all thoroughly washed into the flask.

The resulting copper solution was evaporated to dryness on a hot plate and the last traces of oxides of nitrogen removed by a blast of air. After cooling, 10 cc. of 50 per cent acetic acid were added and boiled until solution was completed, then cooled and made up to 25 cc.

Five cc. of a solution containing 50 grams of potassium iodide per 100 cc. were then added and the solution titrated immediately against standard sodium thiosulfate, 1 cc. of 2 per cent soluble starch being added as indicator after the color had begun to fade. The thiosulfate solution contained about 9.5 grams per liter, equivalent to about 0.0025 gram of copper and was standardized against pure copper.

The amount of maltose equivalent to the copper found was read from a curve prepared in this laboratory from determinations on pure maltose. The maltose per unit of copper oxide obtained by this method is about 96.9 per cent of that obtained by the Munson and Walker method.<sup>2</sup>

<sup>1</sup> U. S. Dept. Agr., Bur. of Chem., *Bull.* 107 (1909), 49.

<sup>2</sup> The difference in the maltose constant of these two methods is due largely to the difference in concentration of the alkali and the substitution of potash for soda. This method was used because it allowed of somewhat more rapid manipulation.

<sup>1</sup> *Biochem. Zeit.*, 10 (1908), 314.

<sup>2</sup> *Coverings, Intern. Sugar Jour.*, 10, 372.

<sup>3</sup> *Jour. prakt. Chem.*, 34, 378.



The weight of plant represented by the 25 cc. of starch solution withdrawn for analysis was:

$$2.5 \text{ g.} \times 5/50 \times 25/105 = 0.0595 \text{ g.}$$

for 5/50ths of the extract were added to the starch and 25/105ths of this digestion were used for analysis. The activity of the samples was expressed by the number of grams of maltose produced by one gram of sample during one hour's digestion at 40° C., that is, the difference in maltose content of control and digestion, divided by 0.0595.

**DETERMINATION OF WATER-SOLUBLE EXTRACT**—For this purpose a glass dialyzing apparatus was used, heavy filter cloth being substituted for the parchment: 25 grams of the dry sample were allowed to digest for eight hours at room temperature with 1000 cc. of water and a little toluene. The cloth and alfalfa were then squeezed as dry as possible and fresh water added. The total time of extraction was 48 hours and five changes of water were made, the sample finally being squeezed out and dried. The difference in weight before and after extraction represented the "water-soluble extract."

#### DISTRIBUTION OF DIASTASE IN THE PLANT

For the purpose of determining the distribution of diastase in the plant, the leaves and stems were examined separately and in every case there was much more diastase in the stems than in the leaves. The average of all separate determinations on laboratory-cured samples showed a ratio of 4.3 to 1, the ratio number varying from 3.3 to 5.2. A sample having 53.6 per cent leaves showed the following distribution:

Sample	Activity of leaves	Stems	Whole
106	0.34	1.75	0.99

Blossoms plucked a few days later showed an activity of 0.35, or about the same as that of leaves. A later separation of hay taken from the mow showed:

Sample	Part of plant	Activity
84	Coarsest stems	1.17
85	Finer stems	0.79
86	Petioles	0.55
87	Leaves	0.21

Whether the presence of tannin is the sole explanation of the low activity of the leaves is doubtful. As there is much more starch in the stems than in the leaves and the plants were actively growing and flowering when cut, it is conceivable that the diastase is present for the maintenance of the sugar-starch equilibrium which seems to exist in the plant juices.

#### FACTORS WHICH AFFECT THE AMOUNT OF DIASTASE DURING THE GROWTH OF THE PLANT

The variation of diastase with light and darkness can be shown by these samples:

Sample	Cut	Cured	Activity	Per cent increase
24	July 8, 8 P.M.	Air-dried	0.57	
27	July 9, 5 A.M.	Air-dried	1.05	84
55	Oct. 6, 6 P.M.	At 50° C.	0.92	
49	Oct. 6, 8 A.M.	At 50° C.	1.25	36

agreeing very closely with the daily changes observed by Brown and Morris with *Tropaeolum*.

Samples were also cut and kept in the dark in water but the relative increase observed in this case was very much smaller; for example:

Sample	Cut	Treatment	Activity	Per cent increase
26	July 9, 5 A.M.	Dried immediately	0.84	
36	July 9, 5 A.M.	Dried in dark for 50 hrs.	0.97	15
43	Oct. 3, 8 A.M.	Dried immediately	0.90	
46	Oct. 3, 8 A.M.	In water in dark 72 hrs.	0.93	3
55	Oct. 6, 6 P.M.	Dried immediately	0.92	
57	Oct. 6, 6 P.M.	In water in dark 22 hrs.	0.95	3

These differences average slightly less than those obtained by Brown and Morris with *Tropaeolum* and are very much less than in their experiments with *Hydrocharis* in which an increase of 153 per cent was observed.

**SEASONAL VARIATIONS**—There seems to be a gradual increase in diastase with advancing summer, followed by a decline at the approach of cold weather. Determinations on the five crops were as follows:

Sample	Crop No.	Date cut	Activity
94	1	May 23, 8 A.M.	0.75
26	2	July 9, 5 A.M.	0.84
147	3	Aug. 2, 8 A.M.	1.51
49	4	Oct. 6, 8 A.M.	1.25
69	5	Nov. 9, 8 A.M.	1.03

The first four samples were cut at the proper time for hay-making; *i. e.*,  $1/10$  to  $3/10$  in bloom. The fifth, perhaps, ought not to be included, as it was only about a foot high when cut—just two days before the first frost. A sample but six inches high and cut at the same time showed an activity of 1.24, indicating that the younger plants are higher in diastase.

#### THE EFFECT OF DIFFERENT CURING CONDITIONS UPON DIASTATIC ACTIVITY

**CHANGES DURING DRYING**—Brown and Morris exposed a number of their samples to chloroform vapor before drying and assumed that the diastase found after chloroforming and drying was the amount present at the time of cutting and that the values obtained by drying without chloroforming were due to a change brought about by the plant activity.

Exposing alfalfa to chloroform vapors caused the plants to wilt as if frozen and the samples so treated, after drying, showed activities from 42 to 84 per cent lower than the controls. Whether the observed difference was due to the chloroform breaking down a certain resistance to the action of some substance which destroys diastase, or to some activity of the living plant producing diastase during drying, is not known. Chloroform itself has a very slight inhibiting action on enzymes. It was found impossible to get concordant results from the fresh plant, either by grinding with sand or grinding in liquid air with and without sand, but in every case the activity was very low. Thus it has been impossible to obtain values for the activity of the fresh plant.

Samples dried at 50° C. in an oven showed but from 79 to 99 per cent of the activity displayed by the samples allowed to dry at room temperature and afterwards placed in the oven at 50°. This was probably due to the warm, humid atmosphere of the ovens, for from some experiments which will be described later it was found that drying in a current of air at 50° increased the diastatic activity as much as 50 per cent. The effect of oven-drying can easily be seen from the following determinations. All samples were cut the morning of May 23rd:

Sample	Temp.	Activity					
		Whole	Per cent	Leaves	Per cent	Stems	Per cent
98	Room	0.88	100	0.29	100	1.43	100
94	50°	0.75	85	0.35	83	1.17	85
95	100°	0.19	22	0.08	28	0.31	22
97	150°	0.03	3	0.015	3	0.06	4

Drying at room temperature in the dark and in full sunlight compared as follows:

Sample	Activity	Decrease Per cent
98 Dried in dark	0.88	
99 Dried in full sunlight	0.68	23

A ground sample exposed to direct sunlight for a year in a closed bottle showed the following loss in activity:

Sample 53	Activity
Before exposure	1.03
After exposure, interior portion	0.76
After exposure, portion next to bottle	0.70

The portion next to the bottle had lost a good share of its color, while the interior portions had lost but little color in comparison. The bleached layer was less than a quarter of an inch in thickness.

The effects of weathering are apparent from the following parallel experiments:

Sample	Treatment	Activity	Loss Per cent
106	Cut and immediately cured at room temp.	0.99	
109	Cut and allowed to lie in the field for a week during which several showers occurred	0.25	75
107	Cut and placed in sunlight, with occasional sprinkling, for two weeks	0.09	91

Even a single, short night rain has considerable effect:

Sample	Treatment	Activity	Loss Per cent
147	Cut morning of Aug. 2nd, after night's rain, dried at 50°	1.51	
150	Cut evening of Aug. 1st, lay in windrow without wilting during rain, was dried following morning at 50°	0.99	34
148	Cut morning of Aug. 1st, thrown into cock in evening, dried following morning at 50°	0.48	69

In comparison, the hays harvested and stacked under the regular season's conditions were very much lower in diastatic activity:

Sample	Activity
82 First crop, some of it had been exposed to rain, stacked	0.14
73 Second crop, stacked	0.50
76 Third crop, stacked	0.57
89 Fourth crop, stored in mow	0.60

Three samples of alfalfa meal obtained in the market showed activities of 0.23, 0.40 and 0.41. These were supposed to be made from selected alfalfa, but were about six months old when analyzed.

#### DIGESTIBILITY—WATER-SOLUBLE EXTRACT

It is natural to ask whether the enzyme content of a hay is of any real value. That can be answered positively only by extensive feeding experiments and even then with difficulty, for the conditions that make for high diastase are also the conditions which are influential in the production of good hay. The buyer who selects choice hay of good color and odor is selecting hay of high diastatic content, for it was noticed throughout this research that diastase and color, odor and flavor went hand in hand.

However, there is good reason to expect a relation between enzyme content and digestibility. It was pointed out that there is much more diastase present in good hay than is needed to transform all the starch present. The alfalfa contains other enzymes as well which may or may not vary in the same manner.

Some work of H. T. Brown<sup>1</sup> indicates that all the cellulose digested by both the horse and pig is digested by the cytase or cellulose-dissolving enzyme in the food, and not by the enzymes secreted by the digestive tract. It is true that much greater action was observed in the animal than *in vitro*, but foods which were deficient or lacking in cytase showed little or no cellulose digestion. It is a common observation that enzymes show greater activity under the conditions obtaining in the digestive tract than under laboratory conditions.

In thirteen series of digestion experiments made under the direction of the Department of Agriculture<sup>2</sup> ten of the trials showed a positive loss due to cooking grain before feeding: that is, "The amount of food required to produce a pound of gain was larger when the food was cooked than when it was fed raw. In some cases the difference was considerable." Soaking the food on the other hand, produced a larger gain in weight per pound of feed than when dry grain was fed. E. F. Ladd<sup>3</sup> found the loss in digestibility of clover hay by cooking to be about the same as that of grain.

As a rough measure of probable digestibility, samples were subjected to autodigestion and the proportion which was soluble in water determined. In nearly every case factors which made for high diastase were found to also make for greater solubility, although the diastase varied much more widely than the solubility. This is illustrated by the following determinations on the first and third cuttings:

FIRST CUTTING			
Sample	Treatment	Activity	Per cent soluble
97	Dried at 150°	0.03	28.4
144	Stacked while damp, somewhat "burnt"	0.10	30.7
95	Dried at 100°	0.19	32.2
92	Dried at 100°	0.41	34.9
108	Dried at 100° (gas turned off after a few hours, finished following day)	0.53	35.8
99	Dried in full sunlight	0.68	38.0
94	Dried at 50°	0.75	36.6
98	Dried in dark	0.88	37.7
106	Dried at room temp.	0.99	40.5

THIRD CUTTING			
Sample	Treatment	Activity	Per cent soluble
148	Exposed to rain in cock, dried at 50°	0.48	32.8
150	In windrow during rain, dried at 50°	0.99	35.4
147	Dried at 50°	1.51	36.8
149	Dried in blast of air, average temp. about 50°	2.27	37.0
151	Dried in blast of air, average temp. about 50°	2.28	37.2

The accompanying curves may illustrate the variations perhaps still better. The three circled points below the "1st cutting" curve represent two samples injured by rain and one sprinkled in the laboratory. In these the loss of diastase has been much greater than the loss of soluble matter. The variations in diastase and solubility of leaves and stems are also shown for the first cutting.

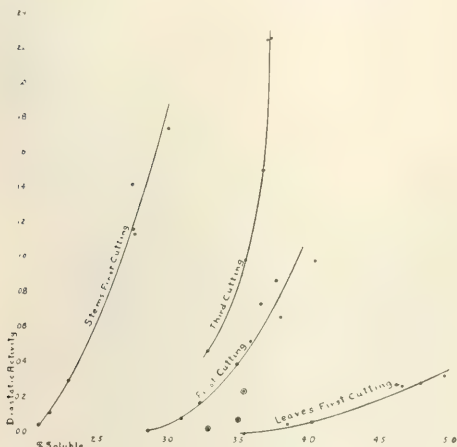
It appears that the percentage of water-soluble substance does not continue to increase beyond a certain point, even when the diastatic activity is much higher and it was thought probable that all the substances acted on by the enzymes might be dissolved out. The leaves and stems of sample 106, which was 40.5 per cent soluble, were digested separately with

<sup>1</sup> Jour. Chem. Soc. Trans., 1892, p. 352.

<sup>2</sup> U. S. Dept. Agr., Farmer's Bull. 22, 25

<sup>3</sup> Ann. Rep. N. Y. Agr. Exp. Sta., 1885, p. 348

cold water as usual and then parallel digestions made with this difference: that after the eight hours at room temperature the whole digestion apparatus was



placed in an oven at 50° for five hours, then heated to boiling and afterwards washed as usual. The results were as follows:

LEAVES	
Activity	
0.34	49.6 per cent soluble at room temperature
	51.6 per cent soluble by heating
	2.0 per cent gain by heating
STEMS	
Activity	
1.75	30.0 per cent soluble at room temperature
	30.4 per cent soluble by heating
	0.4 per cent gain by heating

showing that in the weakly diastatic leaves there were still present substances which could be dissolved out by this treatment, while in the strongly diastatic stems the loss was but one-fifth as great. As this sample was 53.6 per cent leaves and 46.4 per cent stems, this would represent a total solubility of:

40.5 per cent at room temperature
41.8 per cent by heating
1.3 per cent gain by heating

In alfalfa analyzed at the Colorado Experiment Station<sup>1</sup> it was found that a total of 40.53 per cent was soluble by consecutive extractions with four changes of 80 per cent boiling alcohol, 24 hours' digestion with cold water and subsequent treatment with hot water and malt extract. From this it would be inferred that the substances soluble by water and diastase had been pretty thoroughly removed. These substances would include the sugars, dextrans and starch, about half the protein and a part of the coloring matter and mineral constituents.

A partial analysis of sample 89 (4th cutting, field-dried) showed the relative proportion of these constituents in choice hay:

	Leaves	Stems	Whole
Cane sugar.....	1.35	3.90	2.43
Maltose.....	0.20	0.17	0.19
Dextrose.....	1.38	0.30	1.00
Levulose.....	0.78	0.39	0.62
Starch.....	8.34	14.22	10.84
Crude protein.....	25.97	10.42	19.29

<sup>1</sup> Colo. Agr. Exp. Sta., Bull. 124, 12.

#### LOSSES THROUGH HANDLING AND CURING OF HAY

Mention has been made several times of separations of leaves and stems. These separations give some interesting figures as to the losses met with in field curing. The average percentage of leaves found in the laboratory-cured samples, where no losses occurred, was 52.6 per cent. Two samples were allowed to lie in the rain but were dried in the laboratory, so that no diminution in the number of leaves occurred, and both gave 47.4 per cent leaves, or a difference of 5.2 per cent. The average amount of leaves in samples cured in the field under favorable conditions was 46.2 per cent, or a loss of 5.6 per cent. One sample which was cured and stacked after having been exposed to rain in the windrow showed but 35 per cent leaves, or a loss of 17.6 per cent. Assuming that the stems were unaltered by the rain or curing and figuring that all samples originally contained the same proportion of leaves (52.6 per cent), then the rain must have caused a loss in weight of 10 per cent of the total weight of the hay, *this loss all being leaves*. The field curing caused a loss of 12 per cent and both rain and field curing showed a loss of 22.8 per cent in the one sample examined. These figures show loss in weight but not loss in food value, which was much greater, as shown by the following analyses:

Sample	Description	Protein	Sugar	Starch	Fiber
Average	Lab. cured (no loss)	17.83	4.18	10.71	27.50
Average	Field cured (12.0% loss)	13.77	2.25	12.40	30.51
80	Exposed to rain	11.33	0.75	14.12	36.49
	Field cured (22.8% loss)				

Calculating the constituents on the original 100 per cent:

Description	Protein	Sugar	Starch	Fiber
Field cured.....	12.11	1.98	10.91	26.92
Exposed to rain, field cured.....	8.75	0.58	10.91	28.18

which amounts to, in pounds loss per 100 pounds of hay:

Description	Protein	Sugar	Starch	Fiber
Field cured.....	5.72	2.20	0.20 (gain)	0.58
Exposed to rain, field cured.....	9.08	3.60	0.20 (gain)	0.68 (gain)

showing losses of 32 per cent and 51 per cent, respectively in the protein, and 53 per cent and 86 per cent in the sugar content. There must also have been a loss of starch and fiber through the mechanical loss of leaves, but the experimental error in the determination of these substances is relatively large; so, considering other possible errors in sampling, etc., this discrepancy is not surprising.

Fleischmann<sup>1</sup> has shown that in the curing of hay the cellulose content does not change and the starch content drops somewhat when curing takes place slowly. The Kansas Experiment Station<sup>2</sup> has found in weathered hay a calculated total loss of 31.7 per cent, in which 60 per cent of the protein was lost.

W. P. Headden<sup>3</sup> estimated the loss due to weathering of alfalfa at  $\frac{4}{10}$  of the total crop, exclusive of loss by shattering and estimated the loss of leaves and stems by shattering at from  $\frac{1}{8}$  under favorable conditions to  $\frac{2}{3}$  under extreme conditions and repeated handling.

C. Lipscomb<sup>4</sup> in some determinations on timothy

<sup>1</sup> Landwirtschaftlichen Versuchsstationen, 762 (1912), 237-447.

<sup>2</sup> Kans. Agr. Exp. Sta., Bull. 155 (1908), 288-90.

<sup>3</sup> Colo. Agr. Exp. Sta., Bull. 110, 7.

<sup>4</sup> U. S. Dept. of Agr., Farmers' Bull. 362, 26.



hay found from 20 per cent to 40 per cent of "no grade" hay on the outside of stacks which graded No. 1 in the interior, showing the weathering of the outside of the stack to be considerable. Alfalfa is perhaps even more sensitive to weathering than timothy.

Returning to our first figures and assuming the market value of choice alfalfa hay to be \$20 per ton, the loss of from 12 to 23 per cent means a loss of from \$2.75 to \$6.00 worth of hay for every ton harvested; or, for \$20.00 worth harvested the crop should have been worth \$22.75 to \$26.00. This is regardless of the fact that the remaining hay is of less value. Taking the reduced value into consideration, not \$20.00 but perhaps only \$13.00 to \$18.00 would be realized per ton of hay; that is, land which could have produced \$26.00 worth of choice hay may, on account of weathering, produce but \$13.00 worth, giving a loss of 50 per cent. Or, land which could have produced \$22.75 produces but \$18.00, giving a loss of over 20 per cent.

#### METHODS OF CURING AND STORING HAY

Perhaps the most approved method<sup>1</sup> for field curing is to begin cutting as soon as the dew is off in the morning and, if the weather is favorable, to rake and put into small cocks the same afternoon. After allowing to cure in the cocks for several days, the cocks are opened for a short time and the hay taken up before the leaves become dry enough to shatter appreciably. Storing under cover is, of course, preferable, but if the hay is stacked in the open the stack should be well protected with canvas or "slough grass." Curing in the windrow requires less labor, but has the disadvantage that as the leaves dry much faster than the stems a larger proportion is lost by shattering.

Several methods have been suggested for reducing the losses due to weathering and shattering, such as storing in the green state as ensilage, or curing in ventilated stacks or sheds. Any process which requires the removal of the hay from the field while still in the green state necessitates the handling of from three to four times as great a weight of hay, owing to the contained water.

Alfalfa does not lend itself to the making of ensilage as readily as some other fodders, partially owing to the fact that it does not pack well in the silo. The ensilage spoils readily around the edges and the losses due to changes in curing amount to about 10 per cent of the dry weight of the feed. Feed stored in this form must be used within a reasonable time after removal from the silo and, therefore, cannot be easily shipped and marketed.

Curing in ventilated stacks and sheds has met with considerable success when properly conducted. For curing in the stack, poles are erected and the green hay piled in layers two to three feet in thickness, each layer being separated from the lower layer by cross pieces nailed to the poles, thus allowing the free circu-

lation of air during drying. Some sort of a cover is also necessary to prevent excessive weathering of the loosely-piled hay.

In shed curing, sufficient space must be provided so that the whole of one crop may be spread out in a loose layer not exceeding three or four feet in thickness. This crop will be thoroughly cured before cutting-time comes again and the succeeding crops are spread out one above the other in the same manner. Sheds for this purpose must be raised well off the ground and be built of open slats so that the air can circulate freely and allow the evaporation of the water to take place rapidly.

With the hope of being able to cure alfalfa quickly, without losing the enzyme value and at the same time prevent the losses which seemed to be necessary in the curing and handling of hay in the field, an experimental drier was constructed to effect the curing in a current of warm air. As it was found that although heat injures the diastase when the hay is in the green state but exposure to 100° C. after the hay is dry does not affect the diastatic activity appreciably, a system based on the principle of counter-currents ought to accomplish complete drying in a very short time without the loss of any of the valuable properties.

The hay produced by the drier, which will be described later, appeared to be even better than was expected. It had a bright green color equal to that of the growing plant and had the odor and flavor of freshly-cut alfalfa. Shaken up with water, it appeared to have all the properties of the green hay. A sample kept for two years has largely retained these properties, although the color has become, perhaps, a little lighter. The appearance on the whole was far superior to that of any field-cured alfalfa ever examined. Its diastatic activity was 2.27 or an increase of 50 per cent over that of the same hay dried at 50° C. Its solubility in water was, however, but slightly greater.

[NOTE—After these experiments in artificial drying had been started, there was brought to our notice through State Secretary of Agriculture, F. D. Coburn, another method of drying alfalfa by steam heat. The process, briefly described, was this: After the hay is cut and finely chopped, it is passed into a drier which consists of a large cylinder containing pipes for the circulation of steam under pressure. The whole cylinder is revolved and a temperature of about 130° C. is maintained, which is claimed to completely dry the hay in 17 minutes. The process is continuous. A sample of this meal was examined and it was found to have an activity of only 0.40 and but 34.8 per cent was soluble in water. This would place it with the samples which were oven dried at 100° C. in the laboratory and would indicate that the digestibility had been lessened by the heat. It was not as sweet in taste as a good field-cured sample, on account of the inversion of a portion of the cane sugar. The hay had something of a peptone odor and the color was about the same as that of the best field-cured samples.]

After the completion of this work H. B. McClure<sup>1</sup> published a brief outline of some experiments by

<sup>1</sup> LITERATURE ON METHODS OF CURING—U. S. Dept. of Agr., *Farmers' Bull.* 329 and 499; Wis. Agr. Exp. Sta., *Bull.* 121 and Special Bull. "Seeding, Growing and Curing of Alfalfa"; Kansas Agr. Exp. Sta., *Bulls.* 155 and 176; Ohio Agr. Exp. Sta., *Circ.* 91; Miss. Agr. Exp. Sta., *Bull.* 84; "Alfalfa," F. D. Coburn, Orange Judd Co., 1911; "Alfalfa Farming in America," Jos. E. Wing, Sanders Pub. Co., 1909.

<sup>1</sup> U. S. Dept. Agr., Bur. of Plant Indus., *Circ.* 116, 27-31.

T. P. Russell on steam drying of alfalfa and cowpea hay using a plant of the belt conveyor type. A single set of duplicate analyses only was given. This showed the artificially cured hay to be about 5 per cent above the field-cured hay in protein content. In the present work the average difference was found to be about 4 per cent. No cost figures were given but the final conclusion was that such a drier could be made to pay for itself in from one to four seasons.]

#### THE EXPERIMENTAL DRIER

This consisted of a box sixteen feet long and a foot square, built of matched flooring. At one end was fitted another box two and a half feet long and filled with coiled iron wire resistance for the purpose of heating the air by means of the electric current. A centrifugal fan or blower was arranged to force the air over the heating coils and through the drier.

The drying shaft was built about fifteen degrees from the horizontal and four closely-fitting boxes three and a half feet long with ends of wire screen were built to slide easily through the drier and hold the hay. It was found that when the boxes were completely filled with coarsely-chopped hay the resistance to the air was too great to be economical; therefore, a wire screen was placed diagonally through the boxes in such a manner as to allow the air to pass up through a four or five inch layer of hay placed upon the screen. With the boxes all filled in this manner, the air had a velocity of about 160 feet per minute at the open end of the drier. Air velocities were determined by means of a portable anemometer placed in different positions at the open end of the shaft and the average reading taken. Even by using averages, the velocities so obtained were valueless, owing to the eddy currents produced by the uneven distribution of the hay. Kent<sup>1</sup> cites some work to show that the anemometer can give errors as high as 40 per cent when used for measuring velocities in pipes less than two feet in diameter. On this account the anemometer readings were not used in the calculations. Temperatures and humidities were measured by means of wet and dry bulb thermometers placed at intervals along the drier, using the psychrometric table of the U. S. Weather Bureau<sup>2</sup> to convert the observed fall in temperature due to evaporation into percentage humidity. The evaporation of the water caused a drop in the temperature of the air passing through the drier so great that occasionally the temperature of the escaping air was even lower than that of the air at the intake before passing over the heating coils. At these times the escaping air was practically 100 per cent saturated.

When the drier was in operation, a box was removed from the lower or warm end of the shaft every thirty minutes, then all the boxes shifted down one place and a box of fresh hay added at the upper or cold end of the shaft. By this means each box of hay was exposed to a temperature of 25° to 35° C. for a period of half an hour, then moved down to a region of 35° to 45° for a like period, then to 45° to 55° and finally exposed

to a temperature of 55° to 65°, the limit obtainable with the heating arrangement used.

When the drier was operating normally and the boxes all being advanced one position every half hour, a period of two hours was always sufficient to dry the hay so thoroughly that allowing it to stand in the open after removal from the drier caused it to take up moisture.

The results of two half-hour periods will be given as examples. The hay for these runs was cut after sundown on August the 2nd and allowed to lie in a pile covered with canvas until it was chopped preparatory to putting into the drier. The following morning the drier was started on two boxes, and an additional box added every half hour, advancing those already in and removing the dry boxes as fast as necessary to keep up the half-hour additions. After the irregularly-timed boxes had all been removed, the existing conditions were as follows:

Time of run.....	11:00-11:30	1:00-1:30
Temp. of air at intake.....	28.5° C.-83.3° F.	29° C.-84.2° F.
Temp. of wet bulb at intake.....	24 75.2	24 75.2
Equal to a humidity at intake.....	70%	66%
Temp. of air at warm end.....	65° C.-149° F.	64° C.-147° F.
Temp. of wet bulb at warm end.....	30 86	30 86
Equal to a humidity at warm end.....	About 9%	About 9%
Temp. of air at cold end.....	31.5° C.-88.7° F.	33.5° C.-92.7° F.
Temp. of wet bulb at cold end.....	31 87.8	31.5 88.7
Equal to a humidity at cold end.....	96%	85%
Velocity of air through 10" X 10" area, ft. per minute.....	161	237
Volume of air per minute, cu. ft.	112	165

The weights of hay and losses during these runs were:

Box	Weight of green hay Pounds	Weight at 11:00 Pounds	Weight at 11:30 Pounds	Loss Lbs.	Per cent loss	Total per cent loss
1 warm.....	6.00	2.90	2.20	0.70	11.7	63.3
2.....	5.10	3.30	2.30	1.00	19.6	54.9
3.....	4.85	4.45	3.45	1.00	20.6	28.9
4 cold.....	5.40	5.40	4.80	0.60	11.1	11.1
Total.....	21.35	.....	.....	3.30	15.5	.....

	Weight at 1:00 Pounds	Weight at 1:30 Pounds	Loss Lbs.	Per cent loss	Total per cent loss
1 warm.....	5.40	2.65	1.95	0.70	12.9
2.....	4.85	2.50	1.85	0.65	13.4
3.....	5.60	4.50	2.30	1.20	21.4
4 cold.....	4.90	4.90	4.10	0.80	16.3
Total.....	20.75	.....	.....	3.35	16.0

The total losses of moisture in pounds of 3.30 and 3.35 correspond to losses per minute of 0.110 and 0.112 pounds, respectively.

The calculations of results which follow were made by the use of Grosvenor's "Calculations for Dryer Design,"<sup>1</sup> and compared with results obtained by the use of the tables and formulae found in Kent's "Mechanical Engineers' Pocket Book"<sup>2</sup> and the "Psychrometric Tables" of the U. S. Weather Bureau.<sup>3</sup> Values obtained from these sources are marked with an asterisk. (\*)

The air at the fan intake was 83.3° F. and the percentage humidity corresponding to the observed drop of 8.1° F. at that temperature is 70 per cent (\*). One pound of air under these conditions has associated with it 0.0172 pounds (\*) of aqueous vapor. When the temperature of the air is raised to 149° F. the saturation drops to 8.5 per cent (\*); that is, this weight of vapor is but 8.5 per cent of the maximum quantity of aqueous vapor, which could be present at that temperature under atmospheric pressure. A humidity

<sup>1</sup> Trans. Am. Inst. Chem. Eng., 1 (1908), 184.

<sup>2</sup> 1904, p. 491.

<sup>3</sup> Loc. cit.

<sup>1</sup> "Mechanical Engineers' Pocket Book," Wiley & Sons, 1904, p. 491.

<sup>2</sup> U. S. Dept. of Agr., Weather Bureau Bull. 236.

of about 9 per cent (\*) was calculated from the difference between the temperatures of the wet and dry bulbs placed in the warm end of the drier. The humidity at the outlet of the drier was found to be 90 per cent (\*). If the cooling effect while passing through the drier had been due solely to the evaporation of water, the exit temperature should have been 91.5° F. (\*); but in a drier as small as this the loss must have been considerable and the observed temperature was only 88.7° F. At a temperature of 88.7° F. and 96 per cent saturation there is present 0.0278 (\*) pound of water per pound of air, or a gain of 0.0106 pound. To effect the observed evaporation of 0.110 pound of water per minute would, therefore, require 10.37 pounds of air per minute.

One pound of dry air at 88.7° F. occupies 13.82 cu. ft. (\*) and one pound of "saturated" air occupies 14.48 cu. ft. (\*). Interpolation shows that one pound of 96 per cent saturated air would occupy 14.45 cu. ft. Therefore, 10.37 pounds would occupy 150 cu. ft. and 150 cu. ft. per minute would be necessary to effect

The last three columns of the table represent calculations using the average observed inlet temperature and humidity of 84° F. and 70 per cent saturation, outlet humidities of 90 and 85 per cent and the much higher maximum temperatures of 212° F. and 175° F. These calculations are given as a basis for comparison with driers sufficiently long to allow slow and uniform rise to these higher temperatures, thus shortening the time necessary for drying.

For large-scale drying the process would be made continuous either by the use of a horizontal rotating cylinder containing baffles arranged for the agitation of the coarsely-cut hay or by means of a vertical shaft containing open-mesh shelves and some sort of a dumping mechanism. The dumping might be accomplished either by revolving rakes fastened to a central shaft or by a mechanism which would lower and raise the shelves on hinges.

#### COMMERCIAL POSSIBILITIES OF DRYING BY ARTIFICIAL HEAT

No data was at hand for determining the probable

TABLE I—DATA OBTAINED (AND CALCULATED) FROM DRYING EXPERIMENTS

	11:00-11:30 Run		1:00-1:30 Run		CALCULATED		
Rate of evaporation of water, pounds per minute..	0.110	0.110	0.112	0.112	100	100	100
Temperature at intake, ° F.....	83.3	83.3	84.2	84.2	84.0	84.0	84.0
Saturation at intake, per cent.....	70	70	66	66	70	70	70
Equivalent to pounds of water per pound of air...	0.0172	0.0172	0.0166	0.0166	0.0178	0.0178	0.0178
Maximum temperature, ° F.....	149	149	147	147	212	212	175
Resulting humidity, calculated, per cent.....	8.5	8.5	8.7	8.7	...	...	...
Resulting humidity, observed, per cent.....	about 9	about 9	about 9	about 9	...	...	...
Humidity at outlet, per cent.....	96	96	85	85	90	85	90
Temperature at outlet, calculated, ° F.....	...	91.5	...	93.5	103.5	105.5	98
Temperature at outlet, observed, ° F.....	88.7	...	92.7	...	...	...	...
Pounds of water per pound of air at intake.....	0.0278	0.0305	0.0285	0.0292	0.0430	0.0425	0.0356
Pounds of water per pound of air at outlet.....	0.0172	0.0172	0.0166	0.0166	0.0178	0.0178	0.0178
Gain in passing through drier.....	0.0106	0.0133	0.0199	0.0126	0.0252	0.0247	0.0178
Pounds of air per minute necessary to remove water at observed rate.....	10.37	8.27	9.41	8.89	3970	4050	5620
Volume of 1 pound of dry air at outlet temperature, cu. ft.....	13.82	13.90	13.92	13.95	14.20	14.25	14.06
Volume of 1 pound of saturated air at outlet temperature, cu. ft.....	14.48	14.62	14.68	14.72	15.30	15.42	14.98
Difference in volume, cu. ft.....	0.66	0.72	0.76	0.77	1.10	1.17	0.92
Multiplied by per cent saturation equals, cu. ft.....	0.63	0.69	0.65	0.65	0.99	1.00	0.83
Volume of 1 pound of moist air at outlet temperature and saturation, cu. ft.....	14.45	14.59	14.57	14.60	15.19	15.25	14.89
Volume of outgoing air, calculated, cu. ft.....	150.00	120.5	137.1	129.8	60300	61800	83700
Volume of outgoing air, observed, cu. ft.....	112	112	165	165	...	...	...
Specific heat of moist air at intake, B. T. U. per lb. B. T. U. per pound necessary to effect observed rise in temperature.....	0.246	0.246	0.245	0.245	0.246	0.246	0.246
B. T. U. per minute imparted to ingoing air....	16.16	16.16	15.43	15.43	31.5	31.5	22.4
B. T. U. per 100 pounds of water evaporated....	167.8	133.7	145.1	136.3	125000	127600	126000
Volume of air per 100 pounds of water evaporated, cu. ft.....	152500	121700	129500	121600	125000	127600	126000
Pounds of coal per 100 pounds of water evaporated	94200	75200	85500	81700	60300	61800	83700
	28.2	22.5	24.0	22.5	23.2	23.6	23.3

the observed evaporation of 0.110 pound of water per minute.

The specific heat of dry air is 0.2373 (\*) and of water vapor 0.475 (\*) at constant pressure, and one pound of air and 0.0172 pound of water vapor require 0.264 B. T. U. (\*) for each degree of rise in temperature. A change in temperature of from 83.3° F. to 149° F., or 65.7°, would, therefore, require an expenditure of 16.16 B. T. U. for each pound of air used and 10.37 pounds of air would require 167.8 B. T. U. per minute.

There are placed side by side in Table I the calculations using first the observed exit temperature, as representative of the experimental drier, and those using the calculated exit temperature, as representing more nearly a drier of commercial dimensions. The results of both runs recorded are given and it is to be noticed that the difference between calculated and observed exit temperatures was much less in the second run after the drier had been in operation for four hours than after the first run.

efficiency of a drier of commercial size heated by steam. However, the following approximations were made by calculating from assumed values based upon information from several manufacturers of drying machinery and from various other sources.

Assuming the heat equivalent of coal brought at \$2.60 per ton to be 12,000 B. T. U. and that the boiler gave an efficiency of 75 per cent or evaporated 10.3 pounds of water at 100 pounds boiler pressure for every pound of coal and that there was a total radiation and indirect loss of 40 per cent in the heating system, then the total efficiency of the plant would be 0.75 × 60 per cent or 45 per cent and the B. T. U. imparted to the air from every pound of coal would be 45 per cent of 12,000 or 5400 B. T. U. Reducing all calculations to a basis of 100 pounds of water evaporated and dividing the B. T. U. so obtained by 5400, we arrived at values, in the seven different columns, of 28.2, 22.5, 24.0, 22.5, 23.2, 23.6, and 23.3 pounds of coal per 100 pounds of water evaporated.



The amount of moisture in green alfalfa varies considerably. A sample cut during a rain contained 81 per cent moisture while in other samples the moisture content was as low as 60 per cent. The average of those samples dried in the laboratory was nearly 75 per cent. This of course is much greater than would be found in hay cut under ordinary conditions. The samples used for these tests contained about 64 per cent water, while a sample taken at the same time, but dried immediately, contained 74 per cent water, showing a loss of 10 per cent from handling and lying in the pile over night. Mowing, raking and hauling on a bright day would probably show a greater loss.

Assuming the moisture content of a hay to be 75 per cent when it reaches the drier, it would require the evaporation of 6000 pounds of water per ton of dry hay;  $6000 \times 23.2/100 = 1390$  pounds of coal per ton of dry hay. At \$2.60 per ton, this would amount to \$1.81 per ton of hay for heat. To this should be added something like 25 cents per ton for interest and depreciation of plant and about \$1.00 per ton for chopping, power and labor, making a total cost of \$3.06 for drying one ton, dry weight, of hay.

Assuming the moisture content to be 64 per cent, as was found in the trials here shown, the production of one ton of dry hay would require the evaporation of but 3600 pounds of water, using 835 pounds of coal at a cost of \$1.09. Adding to this \$1.25 for interest, power, labor, etc., a total cost of \$2.34 per ton is shown. Although these cost figures are only approximations, they lead to some interesting conclusions.

As it was shown that the total loss in the value of hay due to field curing and handling amounts to from 20 per cent under favorable conditions to 50 per cent under adverse weather conditions, and as the calculated cost for artificial drying is from \$2.35 to \$3.00 per ton, producing only choice alfalfa of uniform grade, it is apparent that artificial drying may be conducted at a profit in districts where the drier can be situated near both field and source of fuel. The alfalfa meal industry has grown to considerable proportions in the last few years and the demand is for well-cured alfalfa of good color. Several alfalfa millers have expressed the opinion that a hay of such dryness could be ground at about half the cost of the average hay, taken from the stack.

Some millers subject their hay to a short, preliminary drying before grinding. A drier run in connection with an alfalfa-grinding plant would be an excellent combination.

This same principle of drying could doubtless be applied to other fodders and perhaps even to small fruits and other farm products which are occasionally damaged by unfavorable weather during the drying season. Among the other fodders to which drying might be applicable might be mentioned the pea vines from the canning factories and the common weed, sweet clover or yellow Melilot. Pea vines are often made into ensilage but as such they have but a limited demand and the canner often has trouble disposing of the enormous quantity of vines which accumulate and become a nuisance. Pea-vine meal has been

used to a certain extent as an addition to alfalfa meal. Young sweet-clover is used as forage to a small extent in Europe but sun curing does not produce a good hay. Drying in an oven at 50°, however, gave a hay of good appearance and flavor. Samples of these plants examined gave analyses as follows:

	Protein Per cent	Diastatic activity	Water solubility Per cent
Pea vines	17.73	0.54	44.2
Sweet clover	18.85	0.03	32.7

The moisture contents of the two plants in the green state were 84.7 per cent and 83.2 per cent and this would probably be the principal drawback in curing them for feed.

#### SUMMARY

I—The diastatic activity of alfalfa is greater in the morning or after a period of darkness than after a period of exposure to light. There is much more diastase present in the plant during the warm, active, growth-producing summer than during the spring or fall. Young plants contain more diastase than older ones.

II—Drying at elevated temperatures in a humid atmosphere decreases the diastatic activity, even though the temperature is only 50°. Drying in a current of air with gradually increasing temperature, on the other hand, increases the activity markedly. Light and weathering in the field tend to destroy the diastase. Rain during curing is very detrimental.

III—Highly diastatic alfalfas generally show a greater solubility in water by auto digestion than samples low in diastase. However, the degree of solubility in water cannot be increased above a certain limit.

IV—The loss in digestible constituents during handling and curing in the field may vary from 20 per cent under favorable conditions to as much as 50 per cent under adverse weather conditions.

V—Curing by artificial heat, using the principle of counter-currents, gives a hay of better color, odor and flavor than can be produced by other means. The hay appears to retain many of the valuable properties of the green plant, which are ordinarily lost in curing.

VI—The cost of artificial drying is estimated to be less than the losses generally sustained in field curing and, therefore, it ought to be possible to conduct drying at a profit when the drier can be located near both field and source of fuel.

The writer desires to acknowledge his indebtedness to the late Robert Kennedy Duncan for helpful direction and valuable advice in connection with this work.

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#### THE ORIGIN OF VANILLIN IN SOILS—VANILLIN IN WHEAT AND IN THE WATER IN WHICH WHEAT SEEDLINGS HAVE GROWN

By M. X. SULLIVAN

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Vanillin, the chief odorous principle of the vanilla pod, the fruit of *vanilla planifolia*, has been reported as present in a number of plants and plant products. The presence of vanillin in plants and its possible

passage into the medium of growth is of great interest since (1) vanillin has been found injurious to plant growth<sup>1</sup> and (2) it has been found in a number of soils.<sup>2</sup> As yet it has not been reported as formed by microorganisms.

Among the plants and plant material in which vanillin has been reported are asparagus sprouts, seeds of white lupine, ilex leaves, dahlia tubers, grain of oats, and roots of couch grass, potato, pine wood, peat, raw beet sugar, and in resins such as Asafoetida and Siam benzoin.<sup>3</sup> It has been found also in orchid flowers exposed to sudden frosts<sup>4</sup> and in the incrusting pigment of sugar cane on warming with dilute acids.<sup>5</sup>

Vanillin or a closely related mother substance, in large or small quantities, seems to be fairly wide-spread in the vegetable world. Accordingly, as a possible explanation of its occurrence in field soils, it became of interest to determine whether or not vanillin could be found in wheat as a type of field crop and in the water in which wheat had grown.

**VANILLIN IN WHEAT**—When wheat seedlings were extracted with hot alcohol (recently distilled) there was obtained on evaporating the alcohol extract a syrupy mass, part of which was soluble in ether. The ether extract was treated with a half saturated solution of sodium bisulfite in the usual way in testing for aldehydes. The bisulfite solution was freed from sulfite by means of dilute sulfuric acid and the excess of sulfur dioxide driven off by passing air through the liquid. After extraction with ether and evaporation of the ether solution a small amount of matter which smelled of vanillin was obtained. This gave the characteristic vanillin color reactions: blue with ferric chloride, green with ferrous sulfate and bromine water, violet with a mixture of hydrochloric and sulfuric acids and acetone water.

With the recognition that wheat contained vanillin, it became of interest to determine how much of the aldehyde was present. For the quantitative estimation recourse was had to the colorimetric method described by Folin and Denis.<sup>6</sup>

For the quantitative determination, 200 g. of wheat seeds were extracted with alcohol and the extract was then treated in the customary way for extracting aldehydes. The final ether extract from the solution freed from bisulfite was evaporated and taken up with warm water. This water solution was treated with equal parts of lead acetate and lead subacetate as long as a precipitate formed. The filtrate or an aliquot part of it was treated with 5 cc. of the phosphotungstic-phosphomolybdic reagent as described by Folin and Denis and after 5 minutes a saturated solution of sodium carbonate was added until the volume of the liquid was 50 or 100 cc. After standing 10 minutes, the solution was filtered and the blue color generated in the reactions compared in a Schreiner colorimeter with that produced by a similarly treated standard

solution of vanillin. The standard was of such a strength that 10 cc. diluted with the reagents to 100 cc. contained 1 mg. of vanillin or 10 parts vanillin per million. The stock solution of vanillin was made, as recommended by Harder,<sup>1</sup> by dissolving 2 g. of vanillin in 200 cc. of 95 per cent alcohol and diluting to 1 liter and then using 10 cc. of this solution to make 200 cc. of the standard solution as needed. Ten cc. of this standard were treated with 5 cc. of the phosphotungstic-phosphomolybdic reagent and then with sodium carbonate as outlined above.

Vanillin was similarly determined (1) in the ether-soluble part of a solution obtained by heating wheat seeds 4 hours on a steam bath with 5 per cent sulfuric acid; (2) in the alcohol extract of wheat bran; (3) in the alcohol extracts of the roots, tops, and seeds of wheat seedlings 5 to 10 days old; (4) in the seed water or the water bathing the seedlings for the first 24 hours; (5) in the root water or the water which bathed the roots for 4 to 10 days with a change of water every two days. The water solutions were concentrated under reduced pressure and extracted with ether. The quantitative results are given in the following table:

TABLE I—VANILLIN IN WHEAT AND IN THE WATER IN WHICH WHEAT SEEDLINGS HAD GROWN

MATERIAL	QUANTITY	VANILLIN Parts per million
Wheat seeds.....	200 and 500 g.	1-6
Wheat seeds digested with 5% H <sub>2</sub> SO <sub>4</sub> .....	200 g.	5-14
Wheat bran.....	200 g.	3(a)
Roots of wheat seedlings.....	1500 seedlings	7-18(a)
Tops of wheat seedlings.....	1500 seedlings	13-16(a)
Seeds of wheat seedlings.....	1500 seedlings	6-8(a)
Seed water.....	4000 cc.	Trace-3
Root water.....	5000 cc.	Trace to 10(a)

(a) Based on weight of original seeds.

The effect of germination on the amount of vanillin in wheat may be seen more clearly in the following experiment where the vanillin in 1717 ungerminated seeds and in the same number of seeds germinated is compared:

TABLE II—VANILLIN IN UNGERMINATED SEEDS AND IN SEEDS, TOPS, AND ROOTS OF SEEDLINGS 5 DAYS OLD

	P. p. m.
Seed.....	3.6
Plant seed.....	7.7
Plant tops.....	15.2 (Based on weight* of 1717 seeds or 58 g.)
Plant roots.....	13.0
WHOLE PLANT....	35.9

The tables show that vanillin occurs free in ungerminated wheat to a slight degree, that it is increased in amount during the early growth of the plant and can pass from the plant to the medium of growth either directly or more probably as a result of cell sloughing and disintegration. Treatment of ground seeds with dilute sulfuric acid increases the amount of vanillin extractable. Accordingly, it would seem that a mother substance of vanillin occurs in wheat and yields vanillin on hydrolysis by acids or in the process of germination.

Coniferin is regarded by many as the mother substance of vanillin. Coniferin gives a blue color with phenol and hydrochloric acid especially in the presence of a little potassium chlorate, gives glyco-vanillin on treatment with potassium permanganate and chromium trioxide, yields vanillin on treatment with chromic

<sup>1</sup> Schreiner and Reed, *Bull.* **47**, Bur. of Soils, U. S. Dept. Agric. (1907); Schreiner and Skinner, *Bull.* **77**, Bur. of Soils, U. S. Dept. Agric. (1911).

<sup>2</sup> E. C. Shorey, *J. Agr. Res.*, **1** (1914), 357.

<sup>3</sup> Abderhalden, *Biochemische Handlexikon*, **1** (1911), 837.

<sup>4</sup> V. Lippmann, *Ber. d. chem. Ges.*, **45** (1912), 3431.

<sup>5</sup> Langguth and Steuerwald, *Chem. Zentr.*, **1912**, I, 83.

<sup>6</sup> *J. Biol. Chem.*, **12** (1912), 239; *This Journal*, **4** (1912), 670.

<sup>1</sup> *This Journal*, **5** (1913), 619.

acid mixture, yields glucose and a resin by boiling with dilute sulfuric acid. From the roots of wheat seedlings there was obtained, by extraction with hot water and hot alcohol and precipitation from alcohol by means of ether, material which gave a greenish blue color with phenol and hydrochloric acid; a blue color with phenol, hydrochloric acid and a little potassium chlorate; a reducing substance on boiling with dilute sulfuric acid. The method of obtaining the material, its reaction with phenol, and the formation of reducing substances on boiling with acid would indicate the presence of coniferin in the wheat roots. Coniferin, it might be said in passing, has been found in the lignified tissue of a number of plants.

Vanillin we have found also in rotten oak wood, in pineapple pulp and parings and in the hot water extract of lawn grass, consisting of blue grass and a small amount of white clover. The amount of vanillin extractable from grass is considerably increased by heating with 5 per cent sulfuric acid for 4 hours on a steam bath. Undoubtedly it occurs to a greater or less degree in many plants either free or in a conjugated form, from which it may be liberated by oxidation and hydrolysis. Its presence in wood and various forms of vegetation would lead to the conclusion that the vanillin in soil has its origin in vegetable debris and to a minor degree also in direct excretion or cell sloughing by growing plants.

SOIL FERTILITY INVESTIGATIONS, BUREAU OF SOILS  
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WASHINGTON

#### AN EXACT AND EASY METHOD FOR PREPARING A NEUTRAL AMMONIUM CITRATE SOLUTION

By J. M. McCANDLESS  
Received August 8, 1914

Since the writer made his official report as Referee on Phosphoric Acid, in 1908 to the Association of Official Agricultural Chemists, there have appeared a number of interesting articles on the subject matter of that report showing how the ammonium citrate solution could be rendered neutral both by physical and chemical methods. All of this work has confirmed the accuracy of the work done, and the conclusions reached by the writer in his original report. As this report was never published in any chemical journal, being printed only in the Proceedings of the A. O. A. C.,<sup>1</sup> and has therefore never been seen by many who are interested in the subject, the writer may be pardoned for reproducing here a part of that report.

PARTIAL REPRODUCTION OF REPORT OF REFEREE ON PHOSPHORIC ACID FOR 1908

"As the referee was to decide whether the various solutions of ammonium citrate sent him were neutral or not, and as scarcely any two chemists can agree upon the exact point of neutrality, whether from lack of sensitiveness of the indicators, or color-blindness on the part of the operators, he decided to make an analysis of each sample according to the method outlined in his last report to the Association, and be guided by those results in deciding upon neutrality.

METHOD OF ANALYSIS.—Twenty-five cc. of each solution were pipetted into a 250 cc. flask, diluted to mark, shaken, and 25 cc. of this solution were pipetted into a distillation flask. To the

solution in the flask, 40 cc.  $N/4$  caustic soda solution were added, and the contents of the flask distilled into 20 cc.  $N/2$  acid, continuing the distillation till the volume of the distillate measured from 65 to 70 cc. The ammonia in the distillate was then titrated by means of  $N/10$  alkali and cochineal. The residue in the distillation flask was washed into an Erlenmeyer, excess of standard acid added, a few drops of phenolphthalein, and the excess acid estimated by  $N/10$  alkali. From the result, the weight of citric acid originally combined with the ammonia was calculated. Calculating from the formula of the pure salt,  $(\text{NH}_4)_2\text{C}_6\text{H}_5\text{O}_7$ , that the ratio of ammonia to citric acid was as 1:3.765, a basis of comparison was established. Results obtained are given in table below:

Number of analyst	Milli-grams of ammonia in 25 cc. of diluted solution =	Milligrams of citric acid in 25 cc. of original solution =	Ratio of ammonia to citric acid	Ratio in neutral salt $(\text{NH}_4)_2\text{C}_6\text{H}_5\text{O}_7$	REACTION WITH CORALLIN
1	113.9	433.2	1:3.803	1:3.765	Neutral
2	109.3	412.8	1:3.775	1:3.765	Alkaline
3	104.9	424.96	1:4.051	1:3.765	Acid
4	113.7	433.9	1:3.816	1:3.765	Neutral
5	110.5	430.08	1:3.891	1:3.765	Slightly acid
6	111.5	436.48	1:3.915	1:3.765	Acid
7	108.7	421.1	1:3.874	1:3.765	Slightly acid
8	104.7	398.7	1:3.808	1:3.765	Neutral
9	102.8	430.7	1:4.189	1:3.765	Acid

"In the above table, all the solutions which showed materially more citric than 3.765 parts to 1 of ammonia, also showed a decidedly acid reaction to corallin.

"It appears that some chemists prepare their ammonium citrate solution by treating the citric acid with excess of ammonia, and then leave the hot solution to neutralize itself, or finally adjust by means of red and blue litmus paper, or corallin. No. 3 in the above table was prepared in this way. The heat of the mixture not only drove off sufficient ammonia to render it neutral, but continued and left it decidedly acid."

The writer has, only in the past few days, had his attention called to the article of Patten and Marti<sup>1</sup> where in referring to the solutions, analyses of which are given in the above table, they use the following language: "The three solutions claimed to be neutral by McCandless contained 44.3 g.  $\text{NH}_3$ , and 168.76 g.  $\text{C}_6\text{H}_5\text{O}_7$  per liter, the ratio being 1:3.809. The results obtained by us conclusively prove that such a solution would be slightly acid, which fact is further substantiated by the ratio of ammonia to anhydrous citric acid being too wide."

Patten and Marti had evidently failed to note the headings of Columns 5 and 6 in the above table, or they would not have attributed to the writer the "CLAIM" that solutions Nos. 1, 4 and 8 were really neutral, since the heading of Column 6 expressly stated that the words "neutral," "acid" and "alkaline" in the column below referred to the reactions with corallin, and the heading of Column 5 showed that the only ratio of ammonia to citric acid which the referee recognized as being neutral was that of 1:3.765.

The method given by Patten and Marti is an interesting and excellent method of preparing a neutral solution. The writer proposes the following exact and easy method of making a neutral solution of ammonium citrate which involves no analyses or distillations, but only a couple of titrations with solutions always ready in every laboratory:

<sup>1</sup> Bur. of Chem., U. S. Dept. of Agr., Bull. 132, 11.

<sup>1</sup> THIS JOURNAL, 6 (1913), 568.



## PROPOSED METHOD

Carefully sample the lot of citric acid on hand, by grinding a sufficient quantity to get an average sample through a coffee or other suitable mill. Mix thoroughly, and weigh 7 g. into a liter flask. Dissolve in water, and dilute to mark. Pipette out 50 cc. or 0.35 g. of the citric acid, and titrate with *N*/10 caustic soda and phenolphthalein. If the acid is pure and uneffloresced, just 50 cc. of *N*/10 alkali will be required. Weigh 1850 g. of pure uneffloresced acid or its equivalent in acid value of effloresced or impure acid into a large bottle or carboy, and cover with 7 liters of cold water. Calculate the exact number of g. of anhydrous citric acid present. Run from a burette 25 cc. of concentrated ammonia into a 500 cc. flask containing cold distilled water. Dilute to mark and mix. Carefully measure 25 cc. of this solution and titrate with *N*/2 acid and methyl orange. Calculate the volume of concentrated ammonia necessary to neutralize the citric acid in the ratio of 1 of ammonia to 3.765 of anhydrous citric acid. (If a stock of approximately 10 per cent ammonia is on hand, it is perhaps preferable to use it instead of concentrated ammonia using, of course, a correspondingly suitable volume of water for the citric acid.) Add the carefully measured ammonia solution to the citric acid in the bottle or carboy, close immediately with a tightly fitting rubber stopper, and shake till the acid is dissolved; allow to stand tightly stoppered until cold, then shake again before removing the stopper. Bring to a gravity of 1.09 at 20° C. The volume of the solution should approximate 10 liters. The accuracy of the solution may be confirmed if desired, by analysis, using either the distillation method already described in this paper, or the method of Patten and Marti,<sup>1</sup> or that of Eastman and Hildebrand.<sup>2</sup>

It was suggested by one of my associates that we attempt to prepare the pure salt, tri-ammonium citrate, and determine the ratio of ammonia to citric acid in it. As anticipated it was found impossible to prepare, by evaporation and crystallization, but by adding to a solution of ammonium citrate made distinctly alkaline with ammonia, a large excess of strong alcohol, a salt was precipitated which on standing over night became beautifully crystalline. The supernatant liquid was filtered off, and the crystals washed thoroughly on the pump with a large excess of strong alcohol; the mass which was a felt of interlaced crystals, was dried quickly by pressure between blotting pads, and a portion dissolved in water; its reaction with corallin was distinctly alkaline, and an analysis of the solution showed the ratio of ammonia to citric acid to be 1 to 3.768. The remainder of the crystals left exposed over night to the summer temperature of the laboratory had entirely changed the nature of its crystalline structure, and a portion of it, when dissolved in water and tested with corallin, was decidedly acid to that reagent and upon analysis showed a ratio of 1 to 3.94. It is evident, therefore, that the normal salt is not entirely hypothetical, that it can be actually

prepared and dissolved in water, and its solution then shows an alkaline reaction to corallin and has very nearly the ratio of 1 of ammonia to 3.765 of citric acid.

There seems little reason to doubt that the neutral ammonium citrate solution which the A. O. A. C. has been prescribing since the date of its organization many years ago, and which able and conscientious chemists have ever since been earnestly trying to make exactly neutral, succeeding sometimes perhaps by accident, but usually only approximating it, was really intended to be a solution of the normal salt. This opinion was expressed by the writer in his report as Referee in the following words: "While the referee has a strong conviction that the only proper method of making the solution is by analysis and calculation of the exact quantity of ammonia and citric acid to be added to it, still he hesitates to urge it officially, as no work has yet been done by any other referee along this line, and because the referee is himself no longer an official chemist." In this opinion he has since been supported by those who have given the most earnest thought and painstaking experiment to the subject, as Patten and Marti, Eastman and Hildebrand and others.

The laboratory with which the writer is identified still makes its solution as prescribed by the A. O. A. C., approximating neutrality as closely as possible by the use of corallin, since that is still one of the legal and official methods, but the writer knows of other chemists who have already adopted the neutralization by analysis, and it is little wonder that under these conditions analyses for available phosphoric acid on tankages and bone meals, and fertilizers containing those ingredients should vary quite widely. Let us hope that the A. O. A. C. at their next meeting will conclude that the subject has been investigated long enough, and take some definite action at that meeting, or else appoint a small committee in whom they have confidence, with power to act in prescribing a method which shall be legal and official after a definite date.

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## THE INFLUENCE OF FINENESS UPON THE AVAILABILITY OF BONE MEAL

By S. S. PRICK  
Received July 6, 1914

It has been thoroughly established that the availability of raw phosphate rock or of basic slag depends primarily on its fineness of subdivision. These two purveyors of phosphoric acid and bones or bone meal comprise the three forms in which insoluble phosphoric acid is supplied in fertilizers. In the case of basic slag, the phosphoric acid exists as a tetra-calcic or a four-lime phosphate. In phosphate rock and bones the phosphoric acid is combined with three parts of lime, and is known as tri-calcic phosphate, to which the general term of bone phosphate is applied.

As superphosphate, phosphoric acid is supplied in a form soluble in water. It is termed available not because after being applied to the soil it remains permanently soluble but because it is fixed in a finely divided

<sup>1</sup> This Journal, 5 (1913), 567.

<sup>2</sup> Ibid., 6 (1914), 577.

form and well distributed. From this it can be logically concluded that the finer the state of subdivision of rock phosphate, and the more thorough its distribution in the soil, the greater will be its availability to the crop. As a matter of fact, the latter condition is directly dependent on the former, since any given quantity of material can be more evenly distributed as its state of fineness increases. The influence of fineness in increasing yields has been demonstrated by the New York Agricultural Experiment Station,<sup>1</sup> and the University of Wisconsin Agricultural Experiment Station<sup>2</sup> has shown that thoroughness of mixing has a decidedly beneficial effect on plant growth.

Truog has published tests showing that the availability of raw phosphate rock is directly influenced by the simultaneous presence of fermenting organic material, this favoring the chemical and biological processes that give rise to carbon dioxide and other agencies which attack the fine rock and ultimately give the material a finer and more uniform distribution through the soil. For this reason the experimental data from phosphate rock experiments cannot be used in arriving at conclusions relative to bone meal action, since here the solvent action is influenced directly by the decomposition of the nitrogenous part of the bone particles, with the accompanying evolution of carbon dioxide and formation of nitric nitrogen. Experimental data, however, is not wanting on this point. The Berlin Agricultural Experiment Station has found that the finer bone meal is ground the better its utilization, coarse meal having but 66 per cent of the action of fine meal, when each contained the same phosphoric acid per cent. The importance of this condition has always been recognized. A hundred or more years ago when bones first began to be used in England, they were applied either unbroken, or later in coarse fragments, at the rate of ten or twelve hundred pounds to the acre. Afterwards, when bone meal came to be manufactured, 600 or 700 pounds of the meal per acre were deemed a sufficient dose, while later 100 or 200 pounds of superphosphate (in which a state of subdivision is reached that would be impossible by grinding) were found to produce the same effect on the same soils and crops.<sup>3</sup>

Storer<sup>4</sup> says: "The fineness of the meal to which bones are ground is a very important consideration. Not so many years ago it was the custom to use crushed bones, . . . but there is no longer any question that fine meal is greatly to be preferred to that which is coarse. The finer the meal, so much the more readily will it putrefy and dissolve in the earth, so much the more quickly can the plants be fed by it, and so much the sooner and the more surely will the value of the crop be increased."

Voorhees<sup>5</sup> also states in positive terms the necessity of fineness of division of bone meal. Many of the experiment stations in the United States attach different values to the phosphoric acid and nitrogen

in fine, medium, and coarse bone meal respectively, but do not in all instances agree in their definitions of these terms. In general, by fine bone meal is signified such as will pass through a sieve with circular holes one-fiftieth of an inch in diameter, and coarse such as will not. The New Jersey Agricultural Experiment Station uses values on this basis as follows: Fine bone meal—nitrogen 19 cents, phosphoric acid 4 cents per pound; coarse—nitrogen 15 cents, phosphoric acid 3.5 cents per pound.<sup>1</sup> The Kentucky Agricultural Experiment Station<sup>2</sup> defines fine bone meal as that which passes through a 25 mesh sieve, and medium as that which passes through a 6 mesh sieve, valuing the phosphoric acid from the former at 4 cents and from the latter at 3 cents per pound. Other stations, particularly that of California, no longer indicate valuations depending on the degree of fineness, since such a gradation is purely arbitrary; nevertheless, they insist on the necessity of such a condition.

There is a limit to which bone meal should be ground on three accounts: (1) When ground too fine to an impalpable powder, known as "floated bone," it is apt to be carried away by the wind when being applied; (2) in this condition it is extremely liable to putrefy, especially in moist air; and (3) there is a question whether its availability is raised for ordinary cultural purposes in a measure commensurate with its extreme fineness. In experiments with various crops, and using bone meal ranging from that passing a 60-inch sieve to that passing through bolting cloth, the New York Agricultural Experiment Station<sup>3</sup> found that within the limits tested, fineness seemed to have little or no influence on availability.

Attempts have been made to measure the availability of raw phosphates by their solubility in various dilute solutions of acids, organic or inorganic, but it has not been found possible to duplicate or even approximately represent conditions in the field with laboratory tests. The solvent action of the soil is being exerted on the insoluble phosphates over a long duration of time, during which a part of the dissolved material is being gradually but constantly removed by the growing crop, and also probably suffering other alterations in character not possible to determine. It may be said that at the present time, there is no chemical method of determining this point in which absolute confidence can be placed.

It has already been stated that bacterial action with its consequent evolution of carbon dioxide and development of acids increases the solubility of rock phosphate, and that this condition exists in the decomposition of bone meal in the soils. In an endeavor to measure the availability of various grades of bone meal, this station has completed a series of tests in which attempts were made to answer the question of availability, and in which the decomposition of the organic matter of the bone was presumed to have a direct relation to the relative availability of the phosphate content.

<sup>1</sup> Bulletin 358, Feb., 1913.

<sup>2</sup> Research Bulletin 20, January, 1912.

<sup>3</sup> B. H. Hite, Bulletin 80, West Virginia Experiment Station, April, 1902.

<sup>4</sup> "Agriculture," Vol. I.

<sup>5</sup> "Fertilizers," 1900, p. 73.

<sup>1</sup> Bulletin 259, September, 1913.

<sup>2</sup> Bulletin 168, December, 1912.

<sup>3</sup> Bulletin 358, February, 1913.

## EXPERIMENTAL WORK

For the purpose of these tests, a commercial bone meal was sifted and divided into four sizes. The sizes and analyses of each lot were as follows:

Number	State of division	Nitrogen Per cent	Phosphoric acid Per cent
1	Less than 40 mesh sieve.....	3.98	17.84
2	From 40 to 60 mesh sieve.....	4.34	22.38
3	From 60 to 120 mesh sieve.....	4.20	23.00
4	Greater than 120 mesh sieve.....	4.09	23.34

## TEST NO. 1

This test was intended to measure the relative rates of ammonification of the nitrogen of the different sizes of bone meal. To Station soil representing 200 g. of dry matter placed in beakers enough of each grade was added to supply 200 mg. of nitrogen; to one lot no bone was added. The bone was thoroughly mixed, and then enough water added to bring the soil to two-thirds saturation.

The beakers and contents were weighed, and every two days during the test were again weighed and water added to replace that lost by evaporation. At stated times one series of each was analyzed for ammonia nitrogen by distilling the whole sample, thoroughly mixed and diluted with water, with recently calcined magnesia into  $N/10$  acid. As the results of the fourth distillation showed a considerable drop in ammonia nitrogen, on the fifth and last test the residue from distillation was transferred to a graduated vessel, cooled, made up to the mark and filtered. In an aliquot of the filtrate, nitrate nitrogen was determined. The results are given in Table I.

Bone meal	Mgs. Ammonia Nitrogen				Mgs. after 18 days as		
	No.	2 days	5 days	9 days	11 days	Ammonia	Nitrate Total
Blank	0	28	0.14	0.14	0.14	0.14	2.1
1	5.46	12.88	6.72	4.20	1.8	29.32	31.12
2	1.96	4.48	2.10	2.38	3.08	13.40	16.48
3	1.40	3.92	3.92	0.98	1.12	10.8	11.92
4	1.76	2.74	2.10	0.78	1.26	15.4	14.66

Up to the fifth day, the rate of ammonia formation was greatest with the finest bone meal and least with the coarsest. On the ninth day a considerable drop in ammonia content is noticed in the lot with the finest material, which progressed until the 18th day. From the figures obtained for nitric nitrogen, this can be explained by the fact that nitrification had started in and was progressing rapidly. On the ninth day the three coarser materials showed practically the same state of ammonification. The final figures for nitrogen, ammonia and nitrate of the 18th day show that decomposition of the bone meal had taken place in the fine material to double the extent it had in the coarser; and that in the coarser materials there were but small and irregular differences.

## TEST NO. 2

This test was a repetition of the previous one with the exception that the soil was kept at a moisture content equivalent to half saturation, and that nitric nitrogen as well as the ammonia was determined in each instance; except that in the first determination, only the ammonia was determined, nitrification not having in two days sufficient opportunity to make much difference, and at the last determination only the nitrates were determined. The results appear in Tables II, III, and IV.

TABLE II - AMMONIFICATION OF BONE MEAL - MGS. AMMONIA NITROGEN							
No.	2	4	7	10	14	17 days	
Blank	1.40	2.31	0.70	0.84	0.70	1.26	
1	8.47	9.80	12.32	7.42	1.26	2.38	
2	7.42	9.94	8.68	5.18	0.70	1.96	
3	6.09	10.08	12.74	4.76	1.12	0.98	
4	5.18	8.12	10.22	2.24	0.70	1.26	

TABLE III - NITRIFICATION OF BONE MEAL - MGS. NITRATE NITROGEN							
No.	4	7	10	14	17	21 days	
Blank	1.40	4.20	4.62	4.62	4.20	3.08	
1	3.92	4.54	9.24	20.30	17.92	24.64	
2	3.22	4.76	10.64	14.70	14.98	15.40	
3	3.08	2.10	7.70	9.66	15.56	14.70	
4	3.08	2.24	9.94	9.94	13.30	14.40	

TABLE IV - MGS. TOTAL NITROGEN AMMONIA AND NITRATE

No.	4	7	10	14	17 days
Blank	6.51	4.90	5.46	5.32	5.46
1	13.72	16.86	16.66	21.56	20.30
2	13.16	13.44	15.82	15.40	16.94
3	13.16	14.84	12.46	10.78	16.54
4	11.20	12.48	12.18	10.64	14.56

In this test, the total water-soluble nitrogen at the end of the 17-day period showed a direct relation to the size of the bone meal; this may be said to hold true for most of the tests, the few irregularities occurring being only what may be usually expected in investigations of this character. It was thought, however, that these irregularities might be explained by the fact that the nitrate nitrogen as formed was accumulating to a much larger degree than usually obtained in nature (amounting to as high as 123 parts per million of dry soil), and perhaps the results would be more regular if the nitrate nitrogen formed were removed at intervals. With this in view, a new series of tests was carried out as follows:

## TEST NO. 3 - LYSIMETER TESTS

For this purpose, galvanized iron containers, with facilities for collecting the drainage, were filled with station soil. The lysimeters were 2 feet in height by eight inches in diameter, the bottoms being perforated and covered with coarse sacking, above which was one inch of animal charcoal, previously digested with acid and washed. Each lysimeter was given 40 pounds of soil. The analysis of this soil by the official acid digestion was:

	Per cent		Per cent
Loss on ignition.....	10.28	Potash.....	0.29
Insoluble residue.....	34.39	Soda.....	1.56
Iron oxide.....	24.96	Sulfuric oxide.....	0.16
Alumina.....	19.56	Phosphoric oxide.....	0.68
Manganese oxide.....	0.15	Chlorine.....	0.01
Lime.....	2.01	Nitrogen.....	0.21
Magnesia.....	5.35		

To each test where bone was added, sufficient was given to represent an application of 100 pounds of nitrogen per acre, amounting actually to 363.5 mg. per lysimeter. In addition to the bone tests, three were carried out with blood and fine ground phosphate rock (60 mesh), alone and together, to see if the effect of the decomposing action of the blood would render more of the phosphate rock soluble, and also to observe whether the presence of the phosphate rock would make any difference in the rate of decomposition of the blood. The blood supplied contained nitrogen at the rate of 100 pounds per acre, while the phosphate rock was equivalent in its phosphoric acid content to the fine bone meal. The plan of the tests was as follows:

## LYSIMETER TESTS

0.3635 g. N per lysimeter (100 lb. N per acre)

No.	MATERIAL ADDED	Grams per lysimeter		Pounds per acre	
		Material	Phosphoric acid	Material	Phosphoric acid
1	(Blank).....	9.133	1.629	2513	448
2	Fine bone meal.....	8.375	1.866	2304	513
3	No. 2 bone meal.....	8.655	1.991	2381	548
4	No. 3 bone meal.....	8.888	2.068	2445	570
5	Coarse bone meal.....	2.872		792	
6	Blood.....	7.218	1.629	1985	448
7	Blood and phosphate rock.....	4.340	1.629	1193	448
8	Phosphate rock.....				

The materials were added by removing from the top of each lysimeter the surface two inches of soil, incorporating thoroughly the respective materials with half of this, replacing in the lysimeters and covering with the remainder of the soil. The bone, etc., was thus one inch below the surface and thoroughly admixed in the second inch. To each lysimeter 500 cc. of water were added, and further additions of water made when the surface of the soil was showing signs of dryness. After three weeks, and every three weeks thereafter, the lysimeters were flushed with 3 liters of water and the percolates analyzed. In the interim between irrigations small applications of water were made when the surface soil showed need of it.

In the analyses, nitrate nitrogen and lime were determined in large aliquots of the percolates, the whole drainage being measured and the results figured to milligrams removed. Por-



tions were concentrated and set aside for phosphoric acid determinations. In all, six percolations were completed, representing a total time of 18 weeks.

In the following tables will be found the amounts of nitrate nitrogen and lime removed at each irrigation.

TABLE V—NITRATE NITROGEN REMOVED (MILLIGRAMS)  
Lysimeter number

Irrigation No.	1	2	3	4	5	6	7	8
1	49.0	56.2	52.7	52.0	62.3	69.4	67.2	91.2
2	23.3	41.2	37.1	33.2	33.7	97.6	81.9	40.5
3	18.1	27.8	24.9	21.1	18.8	90.4	95.7	19.7
4	13.0	20.5	20.3	18.6	16.6	31.4	48.8	9.8
5	17.9	29.0	22.1	22.1	23.0	22.1	27.3	19.4
6	13.6	25.5	20.2	22.5	20.2	17.1	17.3	14.9
Total	134.9	200.2	177.3	169.5	176.4	328.0	335.2	195.5

TABLE VI—CALCIUM OXIDE REMOVED (MILLIGRAMS)  
Lysimeter number

Irrigation No.	1	2	3	4	5	6	7	8
1	47.2	53.5	49.0	44.1	45.3	48.6	53.4	63.6
2	54.7	70.2	37.8	66.1	58.1	85.5	86.3	80.6
3	64.8	79.1	38.8	71.8	67.3	111.6	116.6	95.8
4	61.4	70.0	39.8	73.8	69.3	77.1	94.2	70.4
5	58.4	62.2	46.8	61.3	46.9	66.8	22.2	121.4
6	50.1	36.4	40.0	61.0	48.8	41.1	94.8	82.1
Total	336.6	371.4	222.2	378.1	345.2	430.7	467.5	513.9

It will be noticed that in the first irrigation, the lysimeter to which phosphate rock only was added gave the highest returns for nitrate nitrogen, and of the bone meal tests, the coarsest ranked first in this respect. It is apparent that this discrepancy is due to an unequal condition of the soil at the time of being placed in the lysimeters, which was corrected after the first irrigation. In the following tables, the total amounts of the elements removed in the last five irrigations are reported in terms of pounds per acre:

TABLE VII—POUNDS OF ELEMENTS REMOVED PER ACRE  
(CALCULATED ON SURFACE AREA OF LYSIMETER)

Lysimeter No.	Nitrate nitrogen		Lime		Phosphoric acid	
	Removed	Excess over check	Removed	Excess over check	Removed	Excess over check
1	23.6	...	79.6	...	4.39	...
2	39.6	16.0	87.4	7.8	6.4	2.1
3	34.3	10.7	55.9	9	5.2	0.9
4	32.3	91.7	91.9	12.3	5.4	1.1
5	31.4	7.8	82.5	2.9	6.0	1.7
6	71.1	47.5	105.1	25.5	8.2	0.9
7	73.7	50.1	113.9	34.3	5.1	3.8
8	28.7	5.1	123.8	44.2	5.0	0.7

From this table it again appears that the fineness of division of bone meal is a measure of its rate of decomposition in the soil, based on the formation of nitric nitrogen from the organic matter in the bone. It was thought that the amount of lime found in the percolates might give some indication of the rate at which the lime phosphate was dissolved within the soil, but the results are too irregular to allow any interpretation. This is partly caused by the fact that, as in lysimeter 6, where no lime was added, the rapid nitrification of the blood and the consequent nitrate nitrogen produced, made for an increase in the lime withdrawn from the soil itself. At the same time, it is interesting to note that the greatest amount of lime appeared in the test to which lime phosphate as phosphate rock was added, and in which the nitric nitrogen produced was less than in any other of the tests with the exception of the check. The phosphoric acid determination showed the greatest solubility in the case of the phosphate rock and blood test, and here the lime content is second in quantity to that of the rock alone. In the bone meal, the difference in results is within the limits of experimental error, but the fine bone shows a greater solubility than the coarser. The second size of bone showed a drop below the check in lime and was less in phosphoric acid than the two coarser bones; the lime drop is significant and points to some fault in the soil or its method of packing and nature of drainage, but the nitrogen transformation was apparently not affected.

While not germane to the question, it is nevertheless of interest to compare the results of the blood and rock tests with those

from the bone. Where the phosphate rock alone was employed, an increased nitrification of the soil nitrogen to the extent of 5 per cent is noted. With one exception, all the drainages from this test showed a higher nitrate content than the check. Of the nitrogen added as blood, 47.5 and 50.1 per cents were recovered in the period of 18 weeks as nitric nitrogen, while the best yield from the bone was 16 per cent. Nitrification of the blood nitrogen was accelerated by the addition of phosphate rock just as was the soil nitrogen, but to a lesser extent. More phosphoric acid was found in the test with blood alone than in the check, which points to a solvent effect exerted by the fermenting action of the blood on the soil phosphates.

#### TEST NO. 4

A final test was made with an attempt to measure the amount of phosphoric acid rendered soluble by bacterial action. In this test, quartz sand previously digested with acid and washed with water till free of acid was mixed with the various materials. Fresh station soil was shaken thoroughly with water, allowed to settle for twenty-four hours, and the sand tests moistened with the supernatant liquid. Two series were started, being allowed to stand three and five weeks, respectively. Five grams of the various sizes of bone meal were placed in 200 grams of sand. In two further tests, blood and phosphate rock or phosphate rock alone, were added, in amounts equivalent to the phosphoric acid and nitrogen content of the fine bone meal. At analysis, the contents of the beaker were transferred with water to a filter, and washed through paper until the runnings amounted to 300 cc. The entire filtrate was analyzed for phosphoric acid. In the case of the phosphate rock tests, the filtrate was very turbid. The results, therefore, do not express what was in solution, but represent material in so finely divided a condition that it passed through the pores of filter paper, and went into solution immediately on the addition of acid. The results were as follows:

TABLE VIII—PHOSPHORIC ACID DISSOLVED IN SAND TESTS  
895.5 MG. OF PHOSPHORIC ACID APPLIED

	3 weeks	5 weeks	Total
Fine bone meal	4.0	3.4	7.4
No. 2 bone meal	2.2	3.8	6.0
No. 3 bone meal	2.6	3.7	6.3
Coarse bone meal	1.3	3.1	4.4
Phosphate rock	5.1	7.8	12.9
Phosphate rock and blood	7.5	11.1	18.6

It would appear from these tests that the phosphoric acid in fine bone meal is more available than that passing a 20 mesh sieve by 23 per cent, and almost 70 per cent more available than that passing through a 6 mesh sieve. The two intermediate sizes are about equal, and both superior to the coarsest. The phosphate rock gave, as was expected from the appearance of the filtrate, a considerably greater phosphoric acid content of the filtrate, which was augmented to an important extent by the decomposing action of the blood.

#### SUMMARY

The results of these tests, based on those from the fine bone meal as 100, may be seen from the following comparative tables:

TABLE IX—AMMONIFICATION IN TWO-THIRDS SATURATION

Days	2	5	9	11	18	Average
Bone meal Size No.	100	100	100	100	100	100
1	100	100	100	100	100	100
2	32	34	30	55	49	40
3	22	30	57	21	34	33
4	19	17	30	3	3	23

TABLE X—NITRIFICATION IN HALF SATURATION

Days	3	4	7	10	14	21	Average
Bone meal Size No.	100	100	100	100	100	100	100
1	100	100	100	100	100	100	100
2	85	92	71	93	62	77	82
3	66	92	88	63	34	78	84
4	53	65	64	60	33	62	56

TABLE XI. NITRIFICATION IN LYSIMETERS

Weeks Bone meal Size No.	6	9	12	15	18	Average
1	100	100	100	100	100	100
2	77	70	93	38	55	67
3	58	31	78	38	75	54
4	38	7	48	46	71	46

TABLE XII.—SAND TESTS—WATER SOLUBLE PHOSPHORIC ACID

1.....	100	3.....	85
2.....	81	4.....	60

## CONCLUSIONS

I—The fineness of bone meal determines the rate at which its nitrogenous part will decompose in the soil to ammonia and thence to nitric nitrogen.

II—The solubility of bone phosphate is directly influenced by bacterial action, and an increased ammonia or nitrate decomposition may be held to indicate a more efficient phosphoric acid solvent action.

III—Since there is a limit to which bone meal can be ground to permit of its convenient handling, fine bone meal should possibly be defined as that which passes through a 50 mesh sieve.

IV—Since, however, it is not commercially practicable to prepare so fine a product without also including a considerable proportion of the very fine dust, a standard of fine bone meal of 65 per cent to pass a 50 mesh sieve, and at least 90 per cent of the remainder to pass a 25 mesh sieve is presented as one to which no reasonable objection can be offered by the dealers, and from which satisfactory results will accrue to the crops.

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### A RAPID METHOD FOR THE DETERMINATION OF CAMPHOR AND OF CERTAIN ESSENTIAL OILS WHEN IN SOLUTION IN ALCOHOL

By W. B. D. PENNIMAN AND W. W. RANDALL

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As the result of series of experiments carried out in this laboratory at intervals during several years, a method has been devised for the assay of spirits of camphor and of peppermint, and of the extracts of lemon, orange, peppermint, anise and nutmeg, which appears to be more rapid and much more accurate than any method with which we are familiar. The facts which form the basis of the method may be grouped under three heads, as follows:

1.—Camphor and the several oils enumerated above are completely expelled from solution in alcohol, when these solutions are mixed with from four to ten volumes of a strong solution of calcium chloride.

2.—The separated camphor or oil dissolves with the greatest ease in low-boiling gasoline, an operation with which alcohol, at least in the presence of such a calcium chloride solution, does not interfere.

3.—Within certain fairly wide limits, the volume of the gasoline solution formed is exactly equal to the sum of the volumes of the gasoline itself and the solid camphor (or oil) which has been dissolved.

The method here described is by no means entirely new. Schmatolla<sup>1</sup> noted that when camphor dis-

solves in light petroleum oil, the volume-relation stated in "3" obtains. He employed a burette graduated in tenths cc. as a measuring apparatus, and weighed out the camphor spirit, which was later precipitated by means of saturated sodium chloride solution. We have secured better results by the use of calcium chloride solution, and prefer graduated milk bottles and the use of the centrifuge as means of accurate measurement of small quantities. Arnost<sup>1</sup> used a somewhat similar method to determine camphor in celluloid, correcting for alcohol dissolved. Chittick,<sup>2</sup> we have found since these experiments were made, used a method similar to ours for peppermint, precipitating the oil with water and, by means of a blank, correcting for alcohol dissolved. We have not found water a satisfactory precipitant, and believe that much time can be saved without decrease in accuracy by the use of pipettes and the avoidance of weighings.

The apparatus called for consists simply of several accurate full pipettes, a Babcock centrifuge, and one or more accurately graduated Babcock milk bottles. If the divisions on the neck of the bottle be from 0 to 10, then the graduated portion will contain just 2 cc. With a magnifying glass the volume of a column of supernatant solution in the neck of the bottle can be read with accuracy, probably to 0.008, perhaps to 0.004 cc.

As the volume of gasoline used should not be much less than, nor much more than twice as great as that of the camphor or oil to be dissolved (if the volume-relation mentioned under "3" is to hold good), it is well to work with such quantities that not much over 0.5 cc. of camphor or oil is to be determined. Thus we have found that 5 cc. of the alcohol solution serves well for strengths from 5 to 15 per cent; 10 cc. is probably better for 4 per cent solutions or anything weaker. The quantity of gasoline should in general be somewhat greater than that of the oil.

## METHOD OF ANALYSIS

FOR STRENGTHS BETWEEN 7 AND 15 PER CENT—Pipette 5 cc. of the solution into the Babcock bottle; fill nearly to the neck with clear calcium chloride solution of sp. gr. 1.37; shake, add *exactly* 1 cc. of gasoline (b. p. 40° to 60° C.); shake, fill with the salt solution to near the top of the graduation; stopper tightly; shake violently, and whirl in the centrifuge at high speed for about five minutes. If now the salt solution is still cloudy, shake thoroughly, and whirl again. Read the menisci as in a milk-fat determination; *i. e.*, the lowest point of the lower meniscus and the extreme edge of the upper. For example, suppose the readings are 9.32 and 1.77; the column corresponds to 7.55 (= 1.51 cc.). Of this 5.00 (= 1 cc.) is gasoline, and 2.55 (= 0.51 cc.) is oil. Then  $4 \times 2.55 = 10.20$  = percentage of oil in the extract.

FOR STRENGTHS LESS THAN 7 PER CENT—Use 10 cc. of the solution and a quantity of gasoline not more than twice that of the oil or camphor to be set free;

<sup>1</sup> *Appl. Anal.*, **16**, 290; *Abstr. Chem. Centre.*, **1901**, 1 (20), 1117; *J. Soc. Chem. Ind.*, **20** (1901), 756; Allen's "Commercial Organic Analysis" (new ed.), Vol. IV, p. 200.

<sup>2</sup> *Z. Unter. Nahr. u. Genussm.*, **12** (1906), 532; *Abstr. J. Soc. Chem. Ind.*, **25**, 1169.

<sup>3</sup> *Proc. Assn. Am. Dairy, Food & Drug Off.*, **1913**, p. 160; *Abstr. Chem.*, **8** (1914), 1847.

otherwise the operation is as before. Now, however, the volume of the oil (2.55 in the example given above) must be multiplied by 2 to yield the percentage.

For strengths of 3 per cent or less, the accuracy of the method naturally is not as great as in the case of those first mentioned. To collect without loss in the neck of the Babcock bottle 0.2 cc. of oil and 0.2 to 0.4 cc. of added gasoline (as must be done in the case of a 2 per cent extract), and to read the volume of the resulting solution with accuracy, is not easy; nevertheless we have met with considerable success.

#### RESULTS

**CAMPHOR**—Using a bottle which had been calibrated with the aid of mercury, the following typical results were obtained:

Standard 10 per cent spirit of camphor—5 cc. used with 1 cc. gasoline. Readings: 8.38 and 0.87.  $8.38 - 0.87 = 7.51$ ;  $7.51 - 5.00 = 2.51$ ;  $2.51 \times 4 = 10.04$  per cent.

Standard 5 per cent spirit—10 cc. used with 1 cc. gasoline. Readings: 8.60 and 1.09.  $8.60 - 1.09 = 7.51$ ;  $7.51 - 5.00 = 2.51$ ;  $2.51 \times 2 = 5.02$  per cent.

Sample No. 6826—Rotation indicated 9.93 per cent. 5 cc. used and 1 cc. gasoline. Readings: 10.40 and 2.90.  $10.40 - 2.90 = 7.50$ ;  $7.50 - 5.00 = 2.50$ ;  $2.50 \times 4 = 10.00$  per cent.

Sample No. 6828—Rotation gave no satisfactory result on account of the marked cloudiness of spirit—between 9.00 and 9.40 per cent indicated. 5 cc. used with 1 cc. gasoline. Readings: 9.00 and 1.71.  $9.00 - 1.71 = 7.29$ ;  $7.29 - 5.00 = 2.29$ ;  $2.29 \times 4 = 9.16$  per cent.

Sample No. 6831—Rotation indicated 7.32 per cent. 5 cc. used with 1 cc. gasoline. Readings: 9.08 and 2.27.  $9.08 - 2.27 = 6.81$ ;  $6.81 - 5.00 = 1.81$ ;  $1.81 \times 4 = 7.24$  per cent.

The angles of rotation were determined in all cases in a 200 mm. tube at 20° C. Percentages were calculated on the assumption that under such conditions a 10 per cent camphor spirit shows a rotation of 8.22°.

In order to try out the method, 68 samples were assayed, using milk bottles of all sorts, just as they happened to come from the shelf; probably forty different bottles were thus brought into use. Many of these, on close examination, were clearly seen to be quite inaccurately graduated. Assuming that the percentage strength was actually that deduced from the rotation observed, this method in the 68 assays made, showed an average error of 0.25 per cent; in each of 22 assays the error was less than 0.10 per cent. Other assays with calibrated apparatus indicated that the errors referred to were in large measure to be charged to the inaccuracy of the graduation upon the bottles.

**PEPPERMINT**—Six extracts of peppermint were made from as many peppermint oils, and labeled A, B, C, D, E and F. From experiments made with these extracts, it was found that the laevo-rotations of the oils varied from 21.0° to 28.9°. Assays by this method gave:

SAMPLE	Stated strengths Per cent	Cc. used		Per cent peppermint found
		Extract	Gasoline	
A.....	9.0	5	1.0	9.04
B.....	10.0	5	0.5	9.00
C.....	10.0	5	1.0	9.92
D.....	10.0	5	0.5	10.00
E.....	15.0	5	1.0	15.04
F.....	12.5	5	1.0	12.48
F.....	10.0	5	1.0	10.04

An attempt to make an assay of "C," in which

10 cc. of extract and 1 cc. of gasoline were employed, resulted in the figure 11.10 per cent. Apparently, alcohol, when present to such an extent as this with oil of peppermint, is also taken into solution. Hence it would seem best to restrict the amount of peppermint extract used (when of about 10 per cent strength) to 5 cc.

A 3 per cent extract gave the following results:

Extract Cc.	Gasoline Cc.	Per cent found	Extract Cc.	Gasoline Cc.	Per cent found
10	0.5	3.06	15.0	1.0	3.33
10	0.5	3.00	12.5	0.5	3.23
20	1.0	1.75	12.5	0.5	3.36
15	0.5	2.92			

From a study of these results it would appear that the method will give good results with weak extracts of peppermint, only when the quantity used is not over 10 cc.

Other extracts analyzed are reported below:

SAMPLE	Strength Per cent	Cc. extract	Cc. gasoline	Per cent found
Oil of lemon, A.....	5	10	1.0	4.92
	5	10	1.0	5.04
Oil of lemon, B.....	5	10	1.0	4.82 (a)
	5	10	1.0	4.96
Oil of orange (sweet).....	5	10	1.0	4.96
	5	10	1.0	5.02
Oil of anise.....	3	10	1.0	2.94
	3	10	1.0	2.98 (b)
	3	10	1.5	2.80 (c)
Oil of nutmeg.....	2	10	0.2	1.94
	2	10	0.4	1.88

(a) Here a notable amount of solid precipitated insoluble in gasoline.

(b) Clear solution in gasoline difficult to obtain.

(c) Probably, as the volume-relation, oil: gasoline = 1 : 5 in this case, the limit for accurate results had been passed

It will be noted that, in the case of the oils listed above, extracts of the standard Pharmacopoeial strengths were made as well as several of greater strength. In addition, U. S. P. extracts were prepared from oil of wintergreen (3 per cent), oil of cassia (2 per cent), and oil of cloves (2 per cent). So far, successful results have not been secured with these extracts. Oil of cassia is too insoluble in gasoline, and oil of wintergreen and oil of cloves gave low results, possibly because of the presence of phenolic compounds, for the oils were colored dark red and deep violet, respectively, when shaken with the calcium chloride solution.

SAMPLE	Strength Per cent	Cc. extract	Cc. gasoline	Per cent found
Oil of wintergreen.....	3	10	1.0	2.46
		10	1.0	2.68
		10	0.5	2.38
Oil of cloves.....	2	10	0.2	1.40
		10	0.4	1.40

In many instances in the course of the experiments here described, there was thrown out of solution, by the calcium chloride solution, a notable amount of solid particles only slowly soluble, or entirely insoluble, in gasoline. This material collected as a layer between the two solutions; by thorough shaking and whirling in the centrifuge it could be washed by the gasoline and packed into a thin, flat layer. The question naturally arises in such cases where the lower reading of the gasoline column should be made. We have in general followed the rule that, where the solid material may be regarded as an impurity in the oil—e. g., the green coloring material in extract of peppermint—the gasoline column extends upward from its upper surface; where, on the other hand, the solid material is probably a normal constituent of the



oil, but is not entirely soluble in gasoline, we have read from the lower surface of the solid layer.

So far as our experiments have gone, no solvent other than petroleum oil has been found which possesses the peculiar volume properties mentioned above under headings "2" and "3." In the case of cassia oil, a mixture of equal volumes of gasoline and benzene readily dissolved the oil set free, but a marked contraction of volume appeared to take place on solution. Ordinary kerosene oil will serve in many cases, but in our experience, the low-boiling oils will dissolve essential oils more readily. We have so far noted no case where the volume relations described under "3" above, failed to hold, provided a petroleum oil was employed, and solution took place readily. Other strengths of calcium chloride solution may serve as well as that employed; we have used only the one.

This work is to be continued, and experiments made with other solvents than gasoline. Any results of interest that may be obtained will be published in due time.

#### ADDENDUM

After the foregoing paper had been written and submitted to the editor, a suggestion was made by the Publication Committee of THIS JOURNAL that we endeavor to replace the solvent originally called for (gasoline of b. p. 40° to 50° C.) by some other more readily obtained and more safely handled. A series of experiments was accordingly undertaken, under our direction, by Mr. C. O. Miller, in the hope that a less volatile oil would be found to serve as well as the low-boiling gasoline which we had used. Commercial benzene was distilled and fractions collected:

50°-60°, 60°-70°, . . . . ., 160° to 170°

Mr. Miller, who had not, up to this time, worked with the method described in this paper, was able to check most satisfactorily our results as long as he made use of the 40° to 50° gasoline which we had employed, or of the 50° to 60° benzene fraction, which he had distilled; but as soon as he attempted to employ a benzene boiling above 60°, variations began to make their appearance; the volume relation no longer held good in all cases. As a rule too high results were obtained, and the higher the boiling point of the benzene fraction used, the greater became the error. In addition, with repeated shaking and rewhirling the percentage of essential oil indicated continued to rise, instead of coming, as in earlier experiments, quickly to a final value. It may be that continued shaking and rewhirling caused the alcohol present to dissolve more and more in the higher boiling oils.

As a result of these experiments we are apparently justified in advising the use of a gasoline boiling at or below 60° C. as applicable in the assay by this method of spirits of camphor, and of extracts of lemon, orange, peppermint, anise, and nutmeg. We have therefore changed the boiling point given in the body of this article so as to read 40° to 60° C.

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## STUDY OF THE METHODS FOR EXTRACTIONS BY MEANS OF IMMISCIBLE SOLVENTS FROM THE POINT OF VIEW OF THE DISTRIBUTION COEFFICIENTS. II

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The use of the distribution coefficient in indicating better conditions for the extraction of certain substances from aqueous solution by means of immiscible solvents has been shown in a previous communication.<sup>1</sup> The present paper is a continuation of that work, studying several more of the common methods for extractions and, if better conditions are indicated, suggestions are made which, it is believed, aid in obtaining better results. Also, a further use of the distribution coefficient is suggested in which, if its value is accurately known and conditions are strictly adhered to, it is unnecessary to make successive shakings and separations, but with one extraction and a calculation from the distribution coefficient, the percentage of substance can be determined.

The value of such a study will be seen from a consideration of the large number of alkaloidal extractions that it is necessary to make in some laboratories and, also, of the great variance in directions given by different authors for the determination of the same substances. Many analysts still extract alkaloids several times and then stop to test a small portion of the non-aqueous solvent to ascertain if the material is all extracted. This is unnecessary because these substances always distribute themselves in the same way. The same number of washings that will remove a large portion of an alkaloid will remove a small portion, provided, of course, that the limits of the solubilities are not exceeded in either of the two solvents.

It has been shown that by a determination of the distribution coefficient and a subsequent algebraic calculation the number of washings can be determined for given volumes of aqueous and non-aqueous solvents which are necessary to extract 99.9 per cent of the material in question. The distribution ratio ( $d$ ) is indicated by the expression

$$\frac{\text{Concentration in 10 cc. water}}{\text{Concentration in 10 cc. non-aqueous solvent}} = \frac{C_1}{C_2} = (d)$$

The algebraic expression for the calculation of the number of washings necessary for an extraction is

$$\text{indicated by } \frac{x_n}{x_0} = \left( \frac{e}{c + da} \right)^n, \text{ where}$$

$a$  = volume of aqueous solvent,

$e$  = volume of non-aqueous solvent,

$d$  = distribution ratio, as given above,

$x_0$  = original amount of material to be extracted in the water layer, and

$x_n$  = the amount of material in the water layer after  $n$  extractions.

The expression  $\frac{x_n}{x_0}$  = the fraction of material in the water layer after  $n$  extractions.

For the calculations of ( $d$ ), the solubilities of chloroform and water in each other, except in the case of

<sup>1</sup> THIS JOURNAL, 6 (1914), 315.

strychnine, were assumed to be negligible for our purposes and the volume of each, upon saturation with the other, was taken as that originally used. For ether and water, however, where there seems to be considerable diversity of opinion and, since in the case of ether and water we are seeking an indication of better conditions rather than absolute accuracy, the solubility of ether in 100 cc. of water was assumed to be 8 cc. and of water in 100 cc. of ether to be 2 cc. at 25° C.<sup>1</sup> From a consideration of the work of Herz<sup>2</sup> and others, the volumes of these two solvents, when 100 cc. of water and 50 cc. of ether were mixed and saturated with each other, were taken as 104 cc. and 43 cc., respectively. These are perhaps more nearly the true volumes than the values previously taken (100 cc. water and 42.2 cc. ether). However, the final results are affected but little.

The materials used for determinations were of Merck's best, carefully prepared for analysis and the alcohol, ether, chloroform or other non-aqueous solvents were of U. S. P. strengths. The shakings were made in 200 cc. glass-stoppered bottles in a thermostat regulating at 25° C. to within 0.1° C. variation. The thermostat was so arranged that six bottles could be placed in a rack and turned end over end at a rate of 30-40 revolutions per minute during a time interval of 35-40 minutes. The bottles were then allowed to hang for a short time in the thermostat till the two solvents were clear; a portion of the non-aqueous solution was pipetted off and the material determined. In addition to the data as tabulated in the previous paper the volumes assumed for both aqueous and non-aqueous solvents are inserted so that the data can be more readily recalculated.

It must be admitted at the beginning of this paper that the value of (*d*) is by no means always a constant over very wide variations in concentration but in most cases with the concentrations ordinarily used in the laboratory, the results were found to be very nearly so and certainly can be used to good advantage in this work. A slide rule was thought sufficiently accurate for the calculations of this paper. Where modifications of old methods are suggested it is simply intended to indicate better conditions under which the experiments can be done.

#### ACONITINE

The United States Pharmacopoeia suggests the extraction of aconitine with ether from aqueous solution made alkaline with ammonia. The distribution ratio was run using 100 cc. of water, 5 cc. of NH<sub>4</sub>OH and 50 cc. of ether with the following result:

TABLE I

Wt. aconitine	Wt. found in 25 cc. ether	Wt. in ether layer (Vol. 43 cc.)	Wt. in water layer (Vol. 109 cc.)	( <i>d</i> ) Conc. 10 cc. water. Conc. 10 cc. ether
0.0693	0.0302	0.0508	0.0185	0.143
0.1000	0.0435	0.0748	0.0252	0.142
0.1780	0.0773	0.1330	0.0450	0.134
Average,				0.140

From this, about 1/3 of the aconitine remains in the aqueous layer on one extraction, where equal volumes

<sup>1</sup> In the previous paper these values were assumed to be 1.2 cc. for water in ether and 7.8 cc. for ether in water.

<sup>2</sup> *Ber.*, 31 (1898), 2670.

of the two solvents are used. When 50 cc. of aqueous liquid are washed with 10 cc. portions of ether (14 cc. for the first and 10 cc. for the subsequent washings, assuming that 4 cc. of the first ether portion saturate the aqueous layer) the value of (*d*) would be

$$\frac{0.140 \times 50}{0.140 \times 50 + 10} = \frac{7.0}{17.0} \text{ or } 0.417. \text{ It takes six such}$$

washings,  $\left(\frac{1}{2.4}\right)^6 = \frac{1}{191}$ , to extract more than 99 per cent and eight washings for more than 99.9 per cent of the aconitine present. This would appear to be a fairly good separation but there are other non-aqueous solvents which have a greater solubility for aconitine and are less soluble in water.

From a consideration of these solubilities it was found that chloroform and benzene were better solvents than ether and it was judged that the distribution ratios between these substances and water would be more favorable than in the case of ether. It is difficult, however, to obtain benzene sufficiently free from thiophenes and other impurities which are not volatile and for this reason, attempts with commercial benzene did not meet with much success.

It is difficult to obtain good results where (*d*) is so small but the best set of results, using 100 cc. of water, 5 cc. of NH<sub>4</sub>OH and 30 cc. of chloroform, is given here.

TABLE II

Wt. aconitine	Wt. found in 20 cc. chlor.	Acon. in chlor. layer (30 cc.)	Acon. in water layer (105 cc.)	( <i>d</i> )
0.1030	0.0644	0.0966	0.0064	0.019
0.1463	0.0932	0.1398	0.0065	0.013
0.1784	0.1113	0.1670	0.0114	0.019
Average,				0.017

A very few washings, using even comparatively small volumes of chloroform, would almost completely extract the aconitine. Two extractions from 50 cc. of aqueous solution, containing 5 cc. (1-1) NH<sub>4</sub>OH with 10 cc. portions of chloroform, separate out more than 99 per cent and three extractions more than 99.9 per cent of the alkaloid. It is, moreover, more convenient to use chloroform than ether because the chloroform is heavier than the aqueous solution and, hence, in our ordinary Squibb separatory funnels, can be drawn off without the use of another funnel.

To prove these conclusions on aconitine, samples were weighed out into 50 cc. of aqueous solution which contained 5 cc. (1-1) NH<sub>4</sub>OH and the solution washed with two 10 cc. portions of chloroform.

TABLE III

Wt. aconitine	Total wt. found	Residue in chlor.	Corrected wt. acon.	Percentage found
0.1032	0.1035	0.0010	0.1025	99.3
0.1025	0.1026	0.0010	0.1016	99.1
Calculated,				99.2

Portions of aconitine were tried in the same way using two portions of ether, 14 cc. for the first, allowing 4 cc. for the saturation of the aqueous layer, and 10 cc. for the second. In every case the separatory funnel was shaken for two minutes and several minutes time allowed for the separation of the layers. This set of results appears to be low, however, due, no doubt, to the difficulty in getting anything like a complete separation with the ether.

TABLE IV

Wt. aconitine	Total wt. found	Residue in ether	Corrected wt. acon.	Percentage found
0.2000	0.1570	0.0005	0.1565	78.5
0.2035	0.1592	0.0005	0.1587	78.2

Calculated, 82.6

It is suggested from the above results, then, that aconitine be extracted from 50 cc. of aqueous solution, containing 5 cc. (1-1)  $\text{NH}_4\text{OH}$ , with three 10 cc. portions of chloroform. This will give over 99.9 per cent of the aconitine present.

## ATROPINE

It was found that the distribution ratio of atropine between water and chloroform was very small and that three washings from 50 cc. of aqueous solution with 10 cc. portions of chloroform were quite sufficient for all practical purposes.

## CITRAL IN LEMON OIL

A practical application of the distribution ratio has been made in the determination of (*d*) between lemon oil and 45 per cent alcohol. In the preparation of "Terpeneless" lemon extract, lemon oil is treated with 45 per cent alcohol, the alcohol being supposed to dissolve out all the citral which is considered the active constituent of this kind of lemon flavoring. Varying volumes of lemon oil and 45 per cent alcohol were shaken in 200 cc. bottles, the percentage of citral in the oil being determined before and after the experiment. The pure lemon oil showed, by analysis, 3.61 per cent of citral. The alcohol was carefully made up and checked at  $15.6^\circ \text{C}$ . to be 45 per cent.

TABLE V

Cc. alcohol	Cc. oil	G. citral in oil used	G. citral found in oil	G. citral in alcohol	Wt. in 10 cc. alcohol Wt. in 10 cc. oil
100	50	1.80	1.58	0.22	0.070
150	30	1.08	0.825	0.255	0.062
100	100	3.61	3.34	0.27	0.081

Average, 0.07 or  $1/14$ 

With equal volumes of the oil and 45 per cent alcohol [although (*d*) is not a constant] one part of citral goes into the alcohol and thirteen parts remain in the oil. From this it is apparent that it would be difficult for the manufacturers to get all of the citral. It is well known that it is better to wash precipitates on the filters repeatedly with small portions of wash water than once with a large portion and this principle is equally true of extractions of this kind. If one volume of lemon oil were shaken out with eighteen volumes of 45 per cent alcohol, about 60 per cent of the citral would be obtained, while, if six portions using three volumes for each washing were employed, about 75 per cent of the citral would be extracted.

The distribution ratio for lemon oil and 50 per cent alcohol was also run to see if the concentration of the alcohol greatly affected the results. In this case (*d*) was found to be about 0.2 or  $1/5$ . If one volume of oil is extracted with 18 volumes of 50 per cent alcohol, about 90 per cent of the citral will be extracted. It is better, then, and more economical, to use 50 per cent alcohol for the extraction and to dilute to the proper strength of alcohol later.

## COCAINE

The distribution ratio of cocaine alkaloid between

ether and water was found to be very small, in the neighborhood of 0.01. If 50 cc. of aqueous solution, made alkaline with  $\text{NH}_4\text{OH}$ , are shaken out with 10 cc. portions of ether, three washings extract more than 99.9 per cent of the cocaine alkaloid. It was found that the concentration of  $\text{NH}_4\text{OH}$  does not affect this ratio greatly.

## CODEINE

The distribution ratio of codeine between 100 cc. of water, 5 cc. of  $\text{NH}_4\text{OH}$  and 50 cc. of ether was run with the following result:

TABLE VI

Wt. codeine	Cod. in 25 cc. ether layer	Cod. in ether layer (43 cc.)	Cod. in water layer (109 cc.)	( <i>d</i> )
0.0688	0.0118	0.0203	0.0485	0.943
0.1258	0.0215	0.0370	0.0888	0.947
0.2086	0.0362	0.0622	0.1464	0.928

Average, 0.939 = 1.0

This means that when using equal volumes of water and ether under the above conditions, about as much of the codeine remains in the aqueous layer as goes into the ether layer. Extractions from aqueous solution with ether are impracticable. From a study of the solubilities it would seem that ether should extract the codeine better than it does but with ether it is difficult to prophesy what the value of (*d*) should approximate. The aqueous layer containing several per cent of ether makes a much better solvent for codeine than pure water and nearly as good as ether saturated with water.

Between 100 cc. of water, 5 cc. of  $\text{NH}_4\text{OH}$  and 30 cc. of chloroform, the results with codeine were as given in Table VII.

TABLE VII

Wt. codeine	Cod. in 20 cc. chlor.	Cod. in chlor. layer (30 cc.)	Cod. in water layer (105 cc.)	( <i>d</i> )
0.0738	0.0480	0.0720	0.0018	0.0071
0.1060	0.0691	0.1037	0.0023	0.0063
0.1729	0.1126	0.1689	0.0040	0.0068

Average, 0.0067

Three washings, using 10 cc. of chloroform for each extraction, would remove the codeine as completely as could be desired in the analytical laboratory.

These conclusions were tried by analysis. Fifty cc. of the aqueous solution were washed three times with 10 cc. portions of chloroform:

TABLE VIII

Wt. cod. used	Total residue	Residue of chlor.	Corrected wt. cod.	Percentage found
0.2007	0.2011	0.0010	0.2001	99.7
0.2001	0.2019	0.0010	0.2009	100.3
Calculated.				99.9

Using ether instead of chloroform:

TABLE IX

Wt. codeine	Total residue	Residue of ether	Corrected wt. cod.	Percentage found
0.1997	0.1055	0.0010	0.1045	52.4
0.2000	0.1080	0.0010	0.1070	53.5
Calculated.				45.0

The agreement in the case of ether is not so good but the results show how much better chloroform is for this work than the ether and from these experiments a satisfactory method for the extraction of codeine would be as follows: Dissolve the codeine substance in dilute acid, make up to about 45 cc., neutralize



and add 5 cc. of strong  $\text{NH}_4\text{OH}$ . Extract with three 10 cc. portions of chloroform, shaking two minutes at each extraction and allowing the separatory funnels to stand after each shaking so that the two layers of liquid separate as completely as possible. This method gives 99.9 per cent of the codeine present.

#### CONIINE

Trials were made with coniine to find its distribution ratio. They did not meet with much success, however, due to the failure to obtain results which checked well. Coniine alkaloid is so volatile that when 0.14 g. of this substance was exposed to the laboratory air at the ordinary temperature where there was a slight draft, it lost 93 per cent of its weight in one hour. Even when the alkaloid was changed to the hydrochloride salt consistent results were not obtained. The value of ( $d$ ) was about 0.05, so that three to five washings with 10 cc. portions of ether would be sufficient to remove from 99 to 99.9 per cent of the coniine from 50 cc. of aqueous solution, made alkaline with  $\text{NH}_4\text{OH}$ .

#### MORPHINE

Morphine and its salts present much difficulty when an attempt is made to extract them from aqueous solution because of their insolubility in most non-aqueous solvents. Chemical literature seems to give no solvents which are immiscible with water that serve very satisfactorily for this extraction. Perhaps the best extraction is with a chloroform and ethyl alcohol mixture from a saturated salt solution but with such a method not much over  $\frac{1}{10}$  g. could be extracted, even after six or seven washings, using only a moderate amount of non-aqueous solvent for each extraction.

Schaeffer<sup>1</sup> has shown recently that morphine can be extracted from aqueous solution by means of a mixture of fusel oil and chloroform. The fusel oil must be especially distilled and dried before use. Schaeffer has also shown that commercial methyl alcohol (Columbian Spirits) dissolves morphine in the ratio 1:15, and a mixture of equal volumes of methyl alcohol and chloroform nearly as well. When a 1:1 methyl alcohol-chloroform mixture is shaken with water, however, practically all of the methyl alcohol dissolves in the water, so that this mixture could not be used to extract morphine directly from aqueous solution.

There have been many other ways suggested for the estimation of morphine, mostly for crystallizing the morphine in ether and subsequent weighing or titration. This method and its difficulties for the extraction of this alkaloid are well known. The very great number of modifications of this method and suggestions for new ones indicate that there is a feeling of need for a method which will extract large and small amounts of morphine with equal ease and accuracy and that any information which would help to solve the problem would be welcome to chemists who have morphine to determine.

It is well known that various inorganic salts precipitate the higher alcohols from aqueous solution. Ac-

cording to Linebarger<sup>1</sup> and Frankforter and Frary,<sup>2</sup> potassium carbonate is the only substance which is capable of salting out methyl alcohol, while many salts have been found by various investigators which will salt ethyl alcohol.

The distribution coefficient of morphine was determined between water, nearly saturated with  $\text{K}_2\text{CO}_3$ , and methyl alcohol, also with a 1:1 mixture of methyl alcohol and chloroform. It was found with methyl alcohol alone and water that considerable amounts of  $\text{K}_2\text{CO}_3$  went through into the methyl alcohol and the ability of this liquid to dissolve morphine (as has been noted by Schaeffer) is very much diminished by even small amounts of water. An equal volume mixture of chloroform and methyl alcohol was next tried. Very little water and  $\text{K}_2\text{CO}_3$  dissolved in the mixture. It was found, however, that morphine, under such conditions, did not go into the non-aqueous layer as pure morphine but as a definite mixture of  $\text{K}_2\text{CO}_3$  and morphine, which gave by titration just twice the normal value of morphine. Chastaing<sup>3</sup> has prepared a compound of morphine corresponding to the formula  $(\text{M})_2\text{K}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$ . When the substance above was extracted and dried, a creamy, amorphous solid was obtained which, on standing exposed to the air, changed to a white crystalline condition. Under the microscope at least three distinct crystals were identified, two forms of morphine and one of  $\text{K}_2\text{CO}_3$ . This indicates that the substance is a physical mixture in the solid condition but in all probability a chemical compound in solution. Analysis showed that the composition corresponded very nearly to the formula  $(\text{M})_2\text{K}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$ . This substance could be titrated very readily but in extraction it would be exceedingly difficult to remove the non-aqueous layer without getting small amounts of the aqueous liquid, which, being a concentrated solution of  $\text{K}_2\text{CO}_3$ , would vitiate the results.

For this reason, in determining the value of ( $d$ ), the non-aqueous liquid could not be evaporated and the morphine titrated directly. A portion of the non-aqueous liquid was pipetted off into a small beaker, the chloroform evaporated gently on the hot plate, 25 cc. of water and enough methyl alcohol added to keep the morphine in solution, 5 cc. of a 5 per cent solution of  $\text{BaCl}_2$  added and the precipitated  $\text{BaCO}_3$  allowed to stand and settle. The precipitate was then filtered off and washed four times with 2 cc. portions of the methyl alcohol-chloroform mixture. The filtrate was again evaporated gently on the hot plate until most of the methyl alcohol was removed. This step is necessary, for too large amounts of methyl alcohol interfere with the end point of the titrations. An excess of standard acid was then added and the titrations made in the usual way, using methyl red as an indicator. The volume of each layer was determined in order to make the subsequent calculations of the distribution coefficient. By observing in a narrow cylinder, accurate to 0.1 cc., it was found that when

<sup>1</sup> Linebarger, *Am. Chem. Jour.*, **14** (1892), 380.

<sup>2</sup> Frankforter and Frary, "Studies in Chemistry," Vol. I, Univ. of Minnesota.

<sup>3</sup> Chastaing, *Jahr. die Forsch. der Chem.*, **1881**, p. 928.

<sup>1</sup> *Am. Jour. Pharm.*, **85**, 439.

20 g. of  $K_2CO_3$  were dissolved in 25 cc. of water and this liquid mixed with 25 cc. of the methyl alcohol-chloroform mixture, there resulted 32.0 cc. of aqueous liquid and 23.0 cc. of non-aqueous liquid.

The following results were obtained by this method, using 50 cc. of water, 40 g. of  $K_2CO_3$  and 50 cc. of the chloroform-methyl alcohol mixture.

TABLE X

Wt. morphine used	Wt. found in 25 cc. non-aq. layer	Mor in non-aq. layer (46 cc.)	Mor in water layer (64 cc.)	(d)
0.0660	0.0302	0.0556	0.0104	0.134
0.1205	0.0512	0.0942	0.0263	0.200
0.1943	0.0898	0.1652	0.0291	0.127

Average, 0.154

Although these results are in the same order of magnitude, they are not very constant. The difficulty seemed to be that when the  $BaCO_3$  was precipitated a little of the morphine was carried down and not easily washed out. Titrations were tried without the use of  $BaCl_2$  to get a titration twice the value of the morphine but no more constant results were obtained in this way, although they had about the same average value of (d). If the average value reached above, 0.154 or  $1/6.5$ , is taken for (d) and 50 cc. of aqueous solution shaken out with 20 cc. portions of the 1 : 1 chloroform-methyl alcohol mixture, it would take four washings to remove 99 per cent of the morphine present.

This method, therefore, suggests a possibility that morphine can be determined in this way and that fairly large amounts could be extracted. The above results are recorded for the purpose of indicating a heretofore untried field, that is, the extraction of substances by means of the alcohols which can be nearly quantitatively salted out from aqueous solution. It is unfortunate that in the case of morphine, methyl alcohol can be salted out with only  $K_2CO_3$ , which salt must be completely removed before the morphine can be determined. If a suitable neutral salt could be found for this purpose, no doubt more satisfactory results could be reached.

Trials were made for the distribution ratio between 100 cc. of water, nearly saturated with 35 g. of NaCl, and 45 cc. of a 2 : 1 mixture of chloroform and ethyl alcohol. Table XI shows the results:

TABLE XI

Wt. morphine used	Wt. in 20 cc. non-aq. liquid	Wt. in non-aq. layer (40 cc.)	Wt. in water layer (100 cc.)	(d)
0.0358	0.0085	0.0160	0.0198	0.495
0.0552	0.0111	0.0222	0.0330	0.595
0.0736	0.0175	0.0350	0.0386	0.441
0.0972	0.0194	0.0388	0.0584	0.602

Average, 0.528  
or about  $1/2$

Closely checking results were not obtained here either, the variance probably being due to slight differences in weight of the sodium chloride. If (d) is equal to  $1/2$ , it would take at least seven washings to extract 99 per cent of the total amount of morphine present, using 50 cc. of aqueous solution and 25 cc. portions of the ethyl alcohol-chloroform mixture after the aqueous solution is saturated. This would make a total volume of 175 cc. of non-aqueous solvent and it would, therefore, be a tedious task to extract morphine in this way.

Since the solubility of morphine is somewhat higher

in ethyl alcohol than in chloroform, a 1 : 1 mixture of chloroform and ethyl alcohol was tried, using 33 g. of NaCl, 0.5 cc. of  $NH_4OH$ , 100 cc. of water and 50 cc. of the non-aqueous solvent. The results indicated that the mixture previously used (about 1 : 3) worked better, for, as the alcohol content was increased, the tendency of the NaCl to come through with the morphine increased and this in turn caused much trouble.

The value of (d) was also determined for morphine between water and a 3 : 1 mixture of chloroform and amyl alcohol. The solubility of morphine is more favorable in amyl alcohol but this alcohol boils at such a high temperature that it is hard to remove by evaporation. For this reason, although numerous trials were made, only this one is given here as being the most favorable. One hundred cc. of water, 0.5 cc. of  $NH_4OH$ , 30 cc. of chloroform-amyl alcohol mixture and morphine hydrochloride were used. Since there were no other substances used in the solutions, 20 cc. of the non-aqueous liquid were pipetted off, evaporated and the residue weighed as morphine.

TABLE XII

Wt. (M)HCl	Wt. morphine	Wt. in 20 cc. non-aq. layer	Wt. in non-aq. layer (30 cc.)	Wt. in water layer (100 cc.)	d.
0.0600	0.0455	0.0140	0.0210	0.0245	0.350
0.0787	0.0598	0.0192	0.0288	0.0310	0.324
0.0993	0.0753	0.0225	0.0338	0.0415	0.367
0.1198	0.0910	0.0284	0.0426	0.0484	0.341

Average, 0.345

If the average value of (d) is taken as 0.34, it would take three washings of 20 cc. each of the above mixture to remove 90 per cent of the morphine from 50 cc. of aqueous solution or six washings to remove 99 per cent. This would, of course, be extremely tedious and too long for the analytical chemist.

From a consideration of the formula  $\frac{x_a}{x_o} = \left( \frac{da}{c+da} \right)^n$ ,

it is to be seen that, if the value of (d) is accurately known, it is possible to take only the material from the first extraction for a determination. If (d) is known,

and from that, the value of  $\frac{x_1}{x_o}$  calculated,<sup>1</sup> using the de-

sired volumes of the two solvents, and then the amount of material in the non-aqueous liquid in the first extraction estimated, this should equal  $\left( 1 - \frac{x_1}{x_o} \right)$  of the total material present. Consequently,

if the amount found is represented by (W), the total weight of material will equal  $\frac{W}{\left( 1 - \frac{x_1}{x_o} \right)}$ .

The distribution coefficient, therefore, opens the way to determine, with much less labor, substances which take continued extractions. It might be said, however, that when such determinations are made, the value of (d) should be determined with that set of reagents and somewhere near the same conditions. If results were desired within 1 per cent of the true value, about as accurate as most of our extraction

<sup>1</sup>  $\left( \frac{x_1}{x_o} \right)$  = the fraction of material in the aqueous liquid after one extraction

determinations, this should be of considerable advantage in the commercial laboratory where many such extractions are made.

The conclusions drawn in the preceding paragraph were tested in the estimation of acetanilid and saccharin and later, morphine. The mixtures were made in 150 cc. glass-stoppered bottles and the bottles shaken by hand for ten minutes, the laboratory temperature being kept as nearly 25° C. as convenient. Portions were pipetted off and the materials determined. This checking was not done in a thermostat because the average analytical laboratory does not have a constant-temperature bath. The determinations of acetanilid and saccharin are based upon the values of (*d*) as found in the previous paper on this subject. When acetanilid was shaken with 30 cc. of chloroform and 50 cc. of water, containing 5 cc. (1-1)  $\text{NH}_4\text{OH}$ , 82.3 per cent of the material should go into the chloroform:

TABLE XIII

Wt. acetanilid	Wt. in 20 cc. chlor.	Wt. chlor. layer (30 cc.)	(3) $\times$ 100	Percentage found
0.2017	0.1122	0.1683	0.2044	100.5
0.2013	0.1119	0.1678	0.2019	100.4

When 30 cc. of amyl acetate were shaken up with 50 cc. of water containing saccharin and 2½ cc. of concentrated HCl, 95 per cent of the saccharin should go into the non-aqueous layer:

TABLE XIV

Wt. saccharin	Wt. in 20 cc. am. acet.	Wt. in am. acet. layer (30 cc.)	(3) $\times$ 100	Percentage found
0.1990	0.1279	0.1920	0.2021	101.5
0.2000	0.1290	0.1935	0.2038	101.8

It might be observed that the results here vary with the amount of concentrated HCl used, so that they are good considering the many errors involved.

Weights of morphine hydrochloride were shaken out, using 50 cc. of water, 0.5 cc. of  $\text{NH}_4\text{OH}$  and 30 cc. of the chloroform-amyl alcohol mixture. Under these conditions we should get 63.8 per cent of the morphine in the non-aqueous layer. Although difficulty was experienced in removing the amyl alcohol by evaporation without loss of morphine, the results give an idea of how well the method could be worked.

TABLE XV

Wt. (M)HCl	Wt. morphine	Wt. in 20 cc. "mixture"	Wt. in non-aq. layer	(4) $\times$ 100	Percentage found
0.0775	0.0588	0.0250	0.0375	0.0588	100.0
0.0828	0.0628	0.0264	0.0396	0.0621	98.9

## PICRIC ACID

The solubility of picric acid between water and several immiscible solvents, chloroform, toluene, amyl acetate, etc., is given by Seidel<sup>1</sup> but there are no data given, nor was there any obtained in this investigation, which shows, upon calculation, a value of (*d*) sufficiently small to make a possible quantitative extraction from aqueous solution. It is, moreover, of

interest to know that the expression  $\frac{C_1}{C_2} = d$  does

not hold, nor can the expression  $\frac{C_1}{\sqrt{C_2}} = d$  be applied more than approximately. It is only with the

<sup>1</sup> "The Solubility of Inorganic and Organic Substances," D. Van Nostrand Co.

expression  $\sqrt{\frac{C_1}{C_2}} = d$ , where (*n*) equals 1.65 to 1.95,

depending upon the organic liquid used as the immiscible solvent with water, that (*d*) is equal to a constant.

## QUININE

Between water, made alkaline with  $\text{NH}_4\text{OH}$ , and chloroform, the distribution coefficient of quinine was found to be very small so that three washings from 50 cc. of aqueous solution with 10 cc. portions of chloroform would nearly completely remove the quinine.

## STRYCHNINE

There is much variance of opinion as to the best method for the extraction of strychnine from aqueous solution. Some authors prefer to use chloroform while others use a mixture of ether and chloroform. The United States Pharmacopoeia gives the solubility of strychnine in chloroform as 1-6 and in ether as 1-5500. At first thought it would seem that the value of (*d*) would be very much smaller when a 3:1 mixture of ether and chloroform was used for the extraction instead of chloroform. But in the case of a mixture like ether and chloroform, the ether acts more as a medium and a diluent for the chloroform rather than as a hindrance to the strychnine when dissolving in the non-aqueous layer.

The distribution ratio, using 100 cc. of water, 2 cc. of  $\text{NH}_4\text{OH}$  and 30 cc. of chloroform, is given below. Dried strychnine sulfate was used for these trials.

TABLE XVI

Wt. dry strychnine sulfate	Wt. strychn.	Wt. found in 20 cc. chlor.	Wt. in chlor. layer (29.5 cc.)	Wt. in water layer (100.5 cc.)	( <i>d</i> )
0.0570	0.0498	0.0336	0.0495	0.0003	0.002
0.0949	0.0828	0.0536	0.0820	0.0008	0.003
0.1621	0.1417	0.0956	0.1410	0.0017	0.003
Average,					0.003

In this case, where (*d*) is so small, the solubility of chloroform in water and *vice versa* was taken into consideration. The solubility of chloroform in water is about 0.5 cc. per 100 cc. of water and, hence, the volume of chloroform at equilibrium was assumed to be 29.5 cc. and of water, 100.5 cc.

The results show that (*d*) is very low and that two washings with 10 cc. portions of chloroform would extract 99.9 per cent of the strychnine, provided, of course, that none of the material was lost around the stoppers of the separatory funnels, etc.

With 100 cc. of water, 2 cc. of  $\text{NH}_4\text{OH}$  and 30 cc. of the 1:3 chloroform-ether mixture, the value of (*d*) is somewhat larger.

TABLE XVII

Wt. dry strychnine sulfate	Wt. strychn.	Wt. found in 10 cc. non-aq. liquid	Wt. in non-aq. layer (2.2 cc.)	Wt. in water layer (106 cc.)	( <i>d</i> )
0.0503	0.0440	0.0140	0.0308	0.0132	0.089
0.0587	0.0513	0.0163	0.0359	0.0154	0.089
0.1717	0.1023	0.0330	0.0726	0.0297	0.084
Average,					0.087

One washing, using 10 cc. of the mixture and 50 cc. of aqueous liquid, would extract 66 per cent of the total amount and two washings 99 per cent. It takes four such washings to extract 99 per cent of the strychnine present.

Trials were made to prove these conclusions. Ex-



tractions were made with two 10 cc. portions of chloroform from 50 cc. of aqueous solution, made alkaline with 0.5 cc. of  $\text{NH}_4\text{OH}$ :

TABLE XVIII

Wt. strychnine used	Total wt. found	Corr. for residue in chlor.	Corrected wt.	Percentage found
0.1594	0.1623	0.0015	0.1608	100.8
0.1594	0.1622	0.0015	0.1607	100.8

Calculated, 100.0

Using 50 cc. of water, 0.5 cc. of  $\text{NH}_4\text{OH}$ , one 10 cc. portion of the 3 : 1 ether-chloroform mixture and 4 cc. of ether (allowed for saturating the water) for the first extraction and 10 cc. of the mixture for the second extraction, the following results were reached:

TABLE XIX

Wt. strychnine used	Total wt. found	Corr. for residue in ether-chlor.	Corrected wt.	Percentage found
0.0688	0.0582	0.0010	0.0572	89.7
0.0626	0.0570	0.0010	0.0560	89.5

Calculated, 90.8

We must conclude, then, that chloroform alone is to be preferred in this extraction. It is possible that some authors may have other reasons for using the mixture.

## CONCLUSIONS

I—The distribution coefficients of a number of substances have been studied with a view to finding the best set of conditions under which to make extractions.

II—It has been shown that chloroform serves to extract aconitine and codeine from aqueous solution better than ether. Chloroform extracts strychnine better than mixtures of chloroform and ether, as suggested by many authors, while ether serves very satisfactorily for the extraction of cocaine alkaloid.

III—The distribution of citral between lemon oil and 45 per cent and 50 per cent alcohol has been discussed from this point of view.

IV—A study of the extraction methods for morphine has been made and none has been found to be short and accurate for the analytical chemist.

V—Under morphine, a use of the distribution ratio has been suggested to avoid laborious and continued extractions.

SOUTH DAKOTA FOOD AND DRUG DEPARTMENT  
VERMILION, SOUTH DAKOTA

# LABORATORY AND PLANT

## THE EXPLOSIBILITY OF GRAIN DUSTS<sup>1</sup>

By HAROLD H. BROWN

Received October 8, 1914

As a result of a number of explosions in grain mills and industrial plants in this country and in Europe, and more especially as a result of an explosion in a feed-grinding plant at Buffalo, New York, in June, 1913, by which thirty-three men lost their lives and upwards of seventy were injured, a cooperative movement between milling interests generally and the Bureau of Mines was arranged for the purpose of making a scientific study of the explosibility of grain dusts, and of methods pertaining to the prevention of such explosions. The milling interests were represented in the conduct of the work by Messrs. Lawrence E. Harmon, President of Buffalo Cereal Company; Frank F. Henry, Manager Washburn-Crosby Company; and George P. Urban, Secretary George Urban Milling Company, all of Buffalo, New York.

This work was started August 1, 1913, being placed under the direction of Prof. George A. Hulet, Chief Chemist of the Bureau of Mines. David J. Price was assigned to the field-engineering work, and on February 1, 1914, Dr. H. H. Brown began a laboratory study of the problem.

During the preliminary study thirteen explosions were investigated which have occurred since 1905. Three of these took place in Iowa, three in New York, two in Illinois, and one in Vermont, Indiana, Kansas, Ohio and Texas. These explosions were classified among the various lines of milling as follows: Cereal mills, 4; elevators, 3; feed mills, 2; starch factories, 2; glucose factory, 1; flour mill, 1. It is reported that, as a result of these explosions, at least 78 men were

killed and 119 injured. The total damage to property exceeded \$2,000,000.

Since 1911 four explosions have occurred in Europe, two in dextrine works, one in a provender mill, grinding peas, beans, and wheat, and one in a linseed mill. As a result 47 men were killed and 119 injured.

In order to make a laboratory study of the problem, samples of the following dusts were collected, and the conditions under which they were produced were studied:

- 1—Dusts produced during the process of elevating and handling grain, and known as elevator dusts
- 2—Wheat-flour dusts from rolls, bolters, purifiers, conveyors, packing machines, etc.
- 3—Wheat-flour dusts from beams, rafters, elevator heads, etc.
- 4—Dusts produced during the cleaning of oats
- 5—Dust from grinding white corn
- 6—Dust from grinding yellow corn
- 7—Dust from grinding oat hulls
- 8—Oatmeal dust from packing machines
- 9—Floor dusts from elevator sweeping
- 10—Oat-groat dusts after aspirator

These dusts were first analyzed in the United States Food and Drug Laboratory, Chicago. Determination of moisture, ether extract, proteins, crude fiber, ash, and nitrogen-free extract or carbohydrates, were made, to ascertain, not only the chemical nature of the materials, but also wherein they might differ from the grains from which they originated.

Experiments were then started in the Bureau of Mines, Pittsburgh, to determine the ignition-temperature of these dusts, using the method of Wheeler.<sup>1</sup> This consisted in forcing the dust in a cloud through a

<sup>1</sup> "Report on the Inflammability and Capacity for Transmitting Explosions of Carbonaceous Dust, Liable To Be Generated on Premises, under the Factory and Workshop Acts," 1913. R. V. Wheeler.

<sup>1</sup> Abstract of a Preliminary Report by David J. Price and Harold H. Brown, published by the Millers' Committee of Buffalo, N. Y.

glass tube, 3 inches in diameter and 55 inches long, against a heated platinum coil, which was 15.75 inches from one end of the tube. The temperature of the coil was obtained by a Pt-PtRh thermocouple, having its hot junction within the quartz tube upon which the coil was wound. Using this method, Wheeler



EXPLOSION IN WHEELER'S APPARATUS—No. 61, YELLOW CORN—1150° C. (2102° F.)  
DUST FROM FIRST BREAK IN DRY MILLING, AS RECEIVED

determined the ignition-temperature—temperature of propagation—of many dusts, obtaining results varying from 805° C. for sugar, 960–1035° for starch, 990° for oat husks, 995° for grain (flour-mill), to 1060° for flour and 1100° C. for castor-oil meal. The results obtained upon grain dusts by the author varied



EXPLOSION IN BUREAU OF MINES INFLAMMABILITY APPARATUS  
No. 15, WHEAT—PRESSURE 11.6 POUNDS  
DUST FROM SIDEWALLS OF ELEVATOR, DRIED

from 995° C. for oat and corn elevator dusts, 1015° for feed dust from dust collector, 1020° for ground oat hulls, 1025° for yellow-corn dust, to 1115° for wheat elevator dust and 1235–1270° for flour dusts. Wheeler worked with samples which had been dried at 107° C.; the author used the samples as received from the mill.

While this work gave the relative ignition-temperatures it did not give the lowest temperature of ignition or the relative inflammability. This latter was determined by means of an apparatus developed in the Bureau of Mines. It consists of an explosion flask of about 1400 cc. (85.36 cubic inches) capacity having

two tubulures, a platinum coil, a device for driving a dust cloud against the coil, and a Crosby pressure-gauge for measuring the pressure developed. In each determination 50 mg. (0.00176 oz.) of the dust are forced in a cloud against the coil, which has been previously heated to a known temperature determined by a thermocouple. The temperature is that inside the coil and, therefore, higher than the actual temperature on the outside of the coil. The dust is ignited by the heated

coil and a pressure developed within the flask, which is registered by the gauge. The relative inflammability at any temperature is measured by the difference in the pressures developed within the flask.

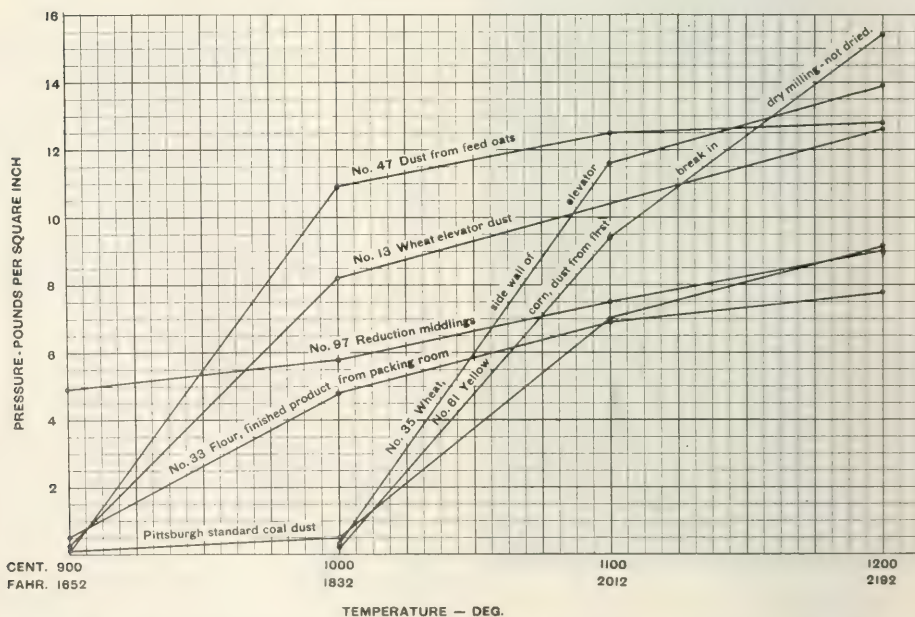
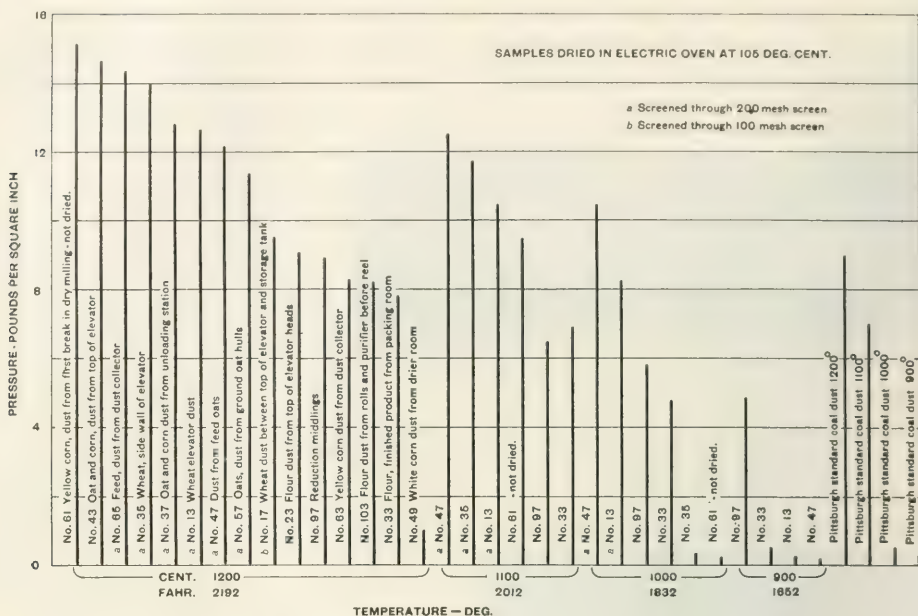
Determinations were made of pressures developed by the different dusts, as received and dried at 105° C., when they were forced against the coil heated to 1200°, 1100°, 1000° and 900° C. As no standard has been taken for carbonaceous dusts, other than coal dust, Pittsburgh standard coal dust, which is very constant in its properties, and which is used as a standard in the Bureau of Mines, was taken as a standard and all determinations run against it and checked against the average value obtained for it at each temperature.

Tables and curves are given which indicate that most, if not all, the grain dusts are more inflammable than Pittsburgh standard coal dust, higher pressures being developed in most cases, and especially so at the lower temperatures. The results also seem to indicate that the dusts from oats and yellow corn are more inflammable than those from wheat or other grain. However, the results are only very preliminary and it is possible that later work will change this supposition, and probably will change the curves, extending them to still lower temperatures.

It is interesting to note the difference in the inflammability of the dried and undried dusts. In nearly every case the pressure developed was appreciably increased after drying. Three are especially noticeable. These gave 0.5 pound pressure or less at 1200° when undried and over 8.0 pounds when dried, Pittsburgh standard coal dust giving 9.0 pounds at the same temperature. This is an indication of what may be expected when the humidity of the air is decreased.

Experiments carried out by the Bureau of Mines<sup>1</sup> have shown that an explosion could be produced when there was only 0.032 ounce of coal dust suspended in each cubic foot of air, or one pound in 500 cubic feet of air. In the experiments of M. J. Taffanel, at the Lievin Experiment Station in France, in one instance as low a weight as 0.023 ounce of coal dust per cubic foot of space was sufficient to produce an

<sup>1</sup> "The Explosibility of Coal Dust," *Bull.* 20, Bureau of Mines, p. 102.



ignition. Since preliminary experiments already conducted indicate that many of the grain dusts have relatively a lower ignition-temperature than many kinds of coal dust and are relatively more inflammable, it may be possible that an ignition of dust of this nature

might be produced with a smaller proportion per cubic foot than is necessary for coal dust.

During the investigations it has developed that the following causes have been assigned to many of the explosions in milling plants in this country and abroad:



- 1—Use of open lights, or naked flames, such as lamps, torches, gas jets, lanterns, candles, matches, etc.
- 2—Property fires.
- 3—Introduction of foreign material in grinding machines.
- 4—Electric sparks from motors, fuses, switches, lighting systems.
- 5—Static electricity produced by friction of pulleys and belts, grinding machines, etc.

The investigation has indicated that a large number of the recent explosions and fires have been caused by the introduction of foreign material into grinding

by those pulp mills using the soda or the "sulfate" process and by the alkali works has long been a serious problem for a number of the mills. In most cases it is not lawful to dump this material into the streams, hence the nearest available low ground is used as a dumping pond. These ponds have in many instances grown to alarming proportions, often using space that is needed for plant extensions.

Another and a more important phase of the problem is that this waste lime itself carries so much potential and actual value that it should not be thrown away after all. It is doubtful if in the average soda pulp mill practice the amount of alkali that goes to the dump will fall below  $1\frac{1}{2}$  per cent calculated as sodium hydrate. This means a value of about 30 cents per ton. The average price paid for lime is probably \$4.00 per ton delivered into the plant. The actual ultimate cost of disposing of lime mud varies at different plants with conditions, but will not fall below 25 cents per ton in any case, all factors being taken into consideration. This waste lime, therefore, represents a possible value of not less than \$4.50 per ton to the average pulp mill or alkali works if burned back to quicklime. In other words, the mill can afford to spend \$4.50 per ton upon a recovery process and still break even.

Some two years ago the writer made a study of the problem simultaneously for a large alkali works and a pulp mill. Burning tests of their sludge were made in a 20-foot test kiln, and all available data were submitted to them. After due consideration, both of these companies have installed recovery plants which are now in successful operation.

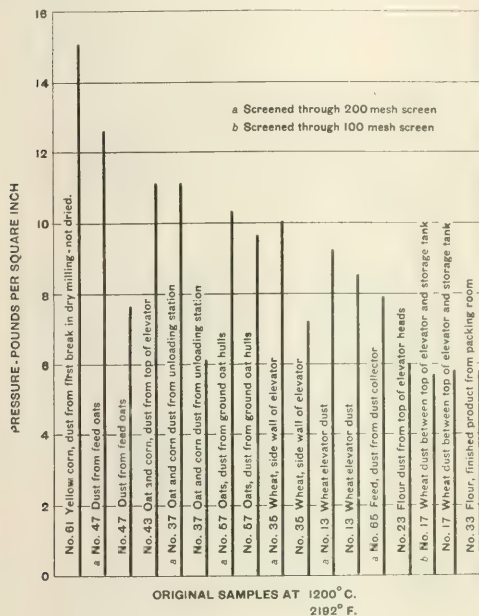
A brief summary of the facts in the case may be of interest to the readers of THIS JOURNAL.

#### STATE OF THE ART

About 1900, one of the large pulp mills installed a rotary kiln 6 ft. in diameter and 60 ft. long preceded by a rotary driver 4 ft. in diameter and 40 ft. long which used the hot gases from the kiln. A 10-ft. producer was used to furnish gas. The results were so unsatisfactory as regards output and fuel economy that the simple 4-ft. driver was later replaced by a Ruggles-Coles drier, with a fan at the outlet of the system to produce sufficient draft. This introduced a dust trouble so serious that the plant has never been able to operate successfully.

About the same time the Western beet sugar plants began to use the rotary kiln for re-burning their spent lime. The results in their case were entirely satisfactory and today a number of kilns are in operation. The size, at first 6 ft.  $\times$  60 ft., has later been increased to 7 ft.  $\times$  60 ft. and even larger. Beet sludge differs from causticizing mud in that it contains less alkali and is of coarser grain, so that filter cakes with as low as 35 per cent water can be produced. These plants use oil as fuel exclusively.

About 1905 one of the alkali works installed a rotary kiln 6 ft.  $\times$  100 ft. for re-burning causticizing mud. The rotary was preceded by a tunnel system of drying the cakes which used waste heat from the kiln. After drying, the cakes were crushed to about 1 in. size and fed to the kiln. The tunnel system seriously inter-



machines. It would appear that a possible means of prevention would be to devise some system by which the foreign material might be removed before it reached the mill. Other preventions suggested are: a complete electric-lighting system, the use of portable electric lamps instead of lanterns or naked lights, the inclosing of the electric-light bulbs in strong wire guards or protectors, and the possible use of vapor-proof globes, and the locating of all fuses, switches, starting boxes, motors, etc., at points where no dust is present. It is also advised to have the receiving bins from the grinding machines as small as practical with the operations, as increased size gives increased space for dust clouds and, therefore, opportunity for a more violent and destructive explosion.

#### THE RECOVERY OF THE SPENT LIME FROM CAUSTICIZING OPERATIONS

By JAMES H. PAYNE

Received September 30, 1914

The disposal of the large quantities of lime sludge that are daily produced in the causticizing operation

fered with the draft and the dry feed produced an excessive amount of dust. This installation is now, however, working satisfactorily, after being remodeled several times.

In Sweden and other European countries several pulp mills using very long kilns 100 to 125 ft. in length, are now reburning their sludge successfully, in spite of the high price they have to pay for fuel.

In the Portland cement industry it is now standard practice to furnace material very similar to lime sludge according to what is known as the "wet process" of cement manufacture. A mixture of limestone and clay is ground to 100 mesh, mixed with 35 per cent water and fed directly to kilns 7 to 9 ft. in diameter and 120 to 180 ft. long. In passing through, it is heated to a temperature of 2700° F. by a jet of powdered coal, oil or gas, which burns the limestone first to lime and then at the high temperature clinkers or fuses the lime with the clay. Experience has shown that a kiln 8 ft.  $\times$  125 ft. will handle 120 tons of mixture on a dry basis per 24 hours with a consumption of 434 lbs. powdered coal per ton, heating same to 2700° F.

It is also now standard practice to burn limestone to quicklime in rotary kilns. The limestone is crushed to about  $\frac{1}{2}$  in. and fed dry through kilns 6 to 8 ft. in diameter and 100 to 150 ft. long, fired with producer gas. A kiln 6 ft.  $\times$  100 ft. will handle 75 tons limestone per 24 hours with a consumption of 210 lbs. coal fed to producer per ton of limestone, this coal also furnishing the power to drive the kiln. Figured to quicklime this is 45 tons of lime produced with 350 lbs. coal per ton.

The standard practice in burning cement mixture by the dry process is for a 6 ft.  $\times$  100 ft. kiln, under similar conditions as in limestone burning, 340 lbs. coal per ton of mixture, or 520 lbs. per ton of clinker produced. The fuel consumption for an 8 ft.  $\times$  125 ft. kiln is about the same, although the capacity is much greater.

#### FUEL REQUIREMENTS

A comparison of these figures shows that the fuel required to burn dry limestone to lime in the rotary kiln is only two-thirds of that required to burn dry cement mixture to cement. Further, we find that the fuel used in the wet process is 30 per cent higher than in the dry. Therefore, the fuel required to burn wet lime sludge may be safely figured to be 30 per cent higher than the figures for dry limestone, or 210 plus 30 per cent, which is 270 lbs. coal per ton dry sludge, or 470 lbs. per ton of quicklime.

It is to be regretted that neither of the installations that have recently been put into operation are provided with independent gas supplies so that the fuel can be measured with sufficient accuracy to verify the above figure. One plant uses natural gas from the service mains, and the other uses producer gas from a main used in common by other furnaces. There is every indication that the estimate is correct. For instance, the natural gas burner was designed amply large for fear the estimate might be low. On starting up, this burner proved to be two sizes too large and had to be replaced by a smaller one.

#### DISTRIBUTION OF COSTS

As only two men are required per shift, over and above those that would be required to place the sludge upon the dump or otherwise dispose of it, it is apparent that the principal item is fuel. As two men can handle a kiln capable of turning out 50 tons lime per day as easily as they can one turning out 25 tons it follows that the labor cost varies with capacity. Fuel charges should be about the same.

Repairs are very low to the moving parts of a rotary kiln, as there is so little to wear out. The life of a kiln is 20 years, with a replacement of the rolls and bearings every two years. Repairs to the lining may be safely assumed to be two relinings a year for half the length of the kiln. A gas producer requires lining about once a year.

Power required for a capacity of 30 tons lime per day is 20 H. P. for the kiln, 5 H. P. for the feeding mechanism, and 5 H. P. steam for blowing the producer.

The total investment for a 30-ton plant would be about \$17,000 and interest and depreciation are figured at 10 per cent.

The cost sheet for a 30-ton plant using producer gas is, therefore, as follows:

Fuel 500 lbs. coal at \$3.00 net ton	\$0.750
Labor 2 men at \$2.50, and 2 men at \$2.00	0.300
Repairs (including one lining per year at \$900)	0.155
Power 30 H. P. at \$40.00 per year	0.110
Interest and depreciation	0.195
Taxes and insurance	0.040
Yard labor, supplies and miscellaneous	0.150
Unforeseen 10 per cent.	0.160
<b>TOTAL COST PER TON LIME</b>	<b>\$1.860</b>

These figures indicate that lime sludge can be re-burned far more cheaply than new lime can be bought, and that a re-burning plant is a good investment even for the alkali works that burn their lime from their own quarries.

#### QUALITY OF THE RECOVERED LIME

There remains the question of quality of the recovered lime. This depends to a great extent upon the quality of the original stone from which it was produced. If the stone is pure and free burning the sludge produced from it is of coarse grain and is also free burning, retaining this property after repeated trips through the circuit. Certain sludges tested by the writer in a 20-foot test kiln have shown a tendency to roll into hard lumps which it was impossible to burn completely to the center of, although nothing unusual could be detected from their analyses or appearance except that they were of extremely fine grain.

It is, of course, impossible to re-burn the same lime indefinitely as it gradually becomes contaminated from constant use, mainly from the lining of the kiln. The customary practice is to introduce a certain quantity of new lime into the circuit periodically. This usually amounts to about 15 per cent of the lime used.

Comparative causticizing and settling tests made upon fresh lime and recovered lime show that recovered lime slakes more slowly and, therefore, causticizes more slowly, but eventually shows the same percentage of causticity. On the other hand it settles much more rapidly, due to its coarser grain and slower hydration. Therefore, it is safe to say that any time

lost in causticizing the liquor is made up in settling time.

#### DUST AND HEAT LOSSES IN BURNING

Contrary to the usual supposition, there is practically no dust produced by a properly designed plant.

At one of the plants now in operation the temperature of the waste gases as they leave the kiln is maintained around 350° F., which is about the limit even for good boiler practice.

#### CONCLUSIONS

The development of the long rotary kiln in the cement industry together with improved methods of filtration and dewatering have made the recovery of the lime sludge from causticizing operations a perfectly simple and feasible proposition. To all soda fiber mills and to most alkali works there is such a wide margin of profit that an installation cannot but be a profitable investment, one likely to pay for itself in two or three years.

202 NORTH CALVERT ST.  
BALTIMORE, MD.

### A LARGE INCUBATOR FOR LABORATORY USE

By F. ALEX McDERMOTT

Received June 29, 1914

In view of the large number of incubators for laboratory use which have been described or listed in the catalogues of dealers in chemical apparatus, it might seem that the design of further apparatus of this type was rather superfluous. However, the apparatus here described has proven so easily and cheaply constructed and set up and so satisfactory that it is believed others may profit from our experience with it.

The first incubator constructed on the plan here described was 5 ft. long, 3 ft. high and 2 ft. deep outside. The walls, including top, bottom and doors, were made of two thicknesses of one-half inch poplar, separated by a one-half inch space; this space was filled with powdered cork. (In constructing further apparatus of this type, the writer would make this space one inch.) Four doors were provided, the two upper ones opening upward until they were flush with the top of the incubator, where they were held by a slotted brass rod and pin, while the two lower doors dropped down and were held pendant from the bottom of the incubator. Median vertical and horizontal cross-pieces in the front of the box were provided, upon which were placed the door catches. These cross pieces were beveled at an angle of 45°, as were also the front edges of the box, and the doors. The doors thus formed a fairly tight joint when closed. An upright was placed against the back, inside, and shelf brackets were placed between this upright and the front vertical cross-piece and also at the ends of the box, inside. The shelves rested upon these brackets. The shelves were made of galvanized iron, perforated with 1/2 inch holes, spaced on about 4-inch centers, and each shelf had two "V" shaped braces on the under side for the sake of rigidity.

The heating and temperature control were both entirely electrical and both were operated on a 110

volt lighting circuit. The heating (for 30° C.) was secured by means of four coils each containing 50 ft. of No. 26 Nichrome wire, two sets, each set of two coils in series, being connected in parallel, the total heating current being about one ampere. In these heating coils or elements, the wire was wound on a frame consisting of two strips 1/2 inch square in cross section and the necessary length (in this case 8 inches) of heavy, hard asbestos board, spaced at the desired distance (14 inches) by means of 3/16 inch bolts; extra nuts on the ends of these bolts served as binding posts for the terminals. Each element was supported by cylindrical, porcelain insulating knobs, such as are used in electrical work. Two elements were fastened to the ceiling and two to the floor of the incubator.

For the temperature control, a 200-ohm main line relay arranged for back contact, was connected in series with a 10 watt carbon lamp and an electrical contact thermometer (Eimer and Amend, No. 6838) constructed for the desired temperature. Of course, the S. M. Co. incubator thermostat may also be used. The total current in the temperature control circuit was about 0.08 ampere. A small 110 volt motor with a 6 inch fan was placed upon the upper shelf at one end of the incubator and connected in parallel with the sets of heating units, to secure more even distribution of temperature. The contact thermometer, which was constructed to close the circuit at 30° C., actually closed it at about 29.75° C. and the temperature in the incubator held, according to a large incubator thermometer placed centrally, at 29.5 to 30.5° C., depending upon the temperature of the room. The above regulation is sufficiently close for many purposes and the range of variation would be considerably reduced in a smaller apparatus. The outside of the box was painted white with two coats of bath-tub enamel over two coats of ordinary white paint.

A number of modifications of the design are possible. The contact thermometer may be obtained so constructed as to close the circuit at any one of a number of points, and a small incubator has been constructed on this principle to hold 45°, 50° or 55° C. A three-point battery switch was provided to cut in and out the different leads. In this case, an ordinary double-wall steam oven was used for the box and a single heating element was used. Instead of the 10 watt lamp, it is better to provide an adjustable resistance, as the sensitiveness and smoothness of operation of the relay may thereby be improved; for this purpose the student's rheostat (made by Jas. G. Biddle, of Philadelphia) has been found satisfactory. A similar resistance may be employed in series with the heating system in order to vary the temperature of the heating coils. The apparatus, as described, works well on direct current. On alternating current it is necessary to adjust very carefully the tension of the relay spring, the distance of the poles from the armature, length of travel of the armature, etc. Attempts to utilize the electrolytic valve rectifier in the temperature control circuit were unsatisfactory. The humming of the relay on alternating current is, of course, objec-



tionable, but by proper adjustment may be largely eliminated. While no trouble was experienced in the breaking of a 110 volt circuit at the contact thermometer, using as low a current strength as here employed, it is advantageous to run the temperature control circuit on the secondary of a small toy or bell-ringing transformer giving 10 or 15 volts.

The total cost of material of the large wooden box incubator was about \$50.00. The labor cost would vary with the circumstances of construction.

MELLON INSTITUTE OF INDUSTRIAL RESEARCH  
UNIVERSITY OF PITTSBURGH  
PITTSBURGH

### A PROPOSED NEW STANDARD LOOP FOR USE IN BACTERIOLOGICAL TESTS OF DISINFECTANTS

By A. D. ST. JOHN  
Received July 7, 1914

The work described herewith was undertaken with a view to obtaining a method of transferring small quantities of a liquid from one containing vessel to another, with rapidity and a fair degree of accuracy; with special reference to the use of such method in the inoculation of broth cultures, as practised in the principal tests of the antiseptic value of disinfectants.

As is pointed out by Duyser and Lewis,<sup>1</sup> the main objection to these tests lies in the unreliability of the "standard loop," which (1) transfers too small a quantity of liquid, *i. e.*, about 0.003 cc. and (2) transfers a quantity which varies as much as 80 per cent from the average.

Tests made in connection with this paper confirmed the second of these objections and indicated that the variation was due to two principal causes:

I—The position of the loop on leaving the surface of the liquid.

II—The rate of removal from the surface.

The variation between removing the loop slowly edgewise, and rather quickly flat to the surface, was from 0.002 to 0.008 g., respectively.

In order to obviate the variation due to position two loops placed with their planes at right angles to one another were tried; and this arrangement gave about equal results when lifted out at any angle perpendicular to the supporting wire, but varied from the result when lifted out with the wire support vertical to the surface of the solution.

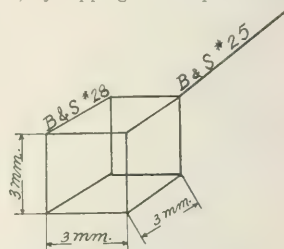
Hence a third loop was added with its plane perpendicular to the wire support, giving three concentric loops, the plane of each at right angles to those of the other two. As a tendency of the drop to break away from the wire at a point farthest from the junction of the wires had been observed, this loop was further modified by changing the spherical shape of the loops to squares, joined at the corners. The loop, or rather cage, thus formed, has the appearance of the outline of a cube, supported by a wire from one corner, and measuring about 3 mm. on an edge. The corners should be welded rather than twisted. The wire of the cube is conveniently made of No. 28 B. and S. Pt wire, and that of the support of No. 25.

This last described loop gave drops varying in weight

from about 0.019 to 0.021 g., according to the angle at which it was lifted from the solution; while the most unfavorable results obtained, varying the rate of lifting out from as slowly as possible, to a quick jerk, was from 0.017 to 0.023 g., respectively; while with ordinary care, several consecutive results of from 0.020 to 0.021 g. were obtained.

Up to this point the measurement of the drop was made by hanging the wire quickly on the balance and weighing by swings. Only slight error was caused by evaporation, as the drop was rather large.

The results with the cube-shaped loop appeared, however, to justify further trials, and tests were now made according to the method of Duyser and Lewis (above), *i. e.*, by dipping out drops of a strong iodine



solution, placing in distilled water, and titrating, using dilute thiosulfate. Eight consecutive tests gave the following ratio:

	Thiosulfate cc.		Thiosulfate cc.
1.....	35	5.....	38
2.....	36	6.....	35
3.....	36	7.....	36
4.....	35	8.....	36

Putting the mean, 35.9 = 100.0, we get a maximum variation of 6 per cent.

It will also be noted that the volume of the drop carried by this loop is about 0.020 cc., or over six times the volume given by Duyser and Lewis as that of the present "standard loop," thus overcoming largely the first objection advanced by them in the article quoted.

It would therefore appear that a loop such as the one described above would eradicate some of the difficulties at present encountered in making determinations of the antiseptic value of disinfectants by the methods mentioned.

The valued aid of Mr. Walter Erlenkotter, of this laboratory, in connection with the preparation of this paper, is gratefully acknowledged by the author.

STANDARD TESTING LABORATORY  
BOARD OF ESTIMATES AND APPORTIONMENT  
NEW YORK CITY

### NOTE ON SUBSTITUTE FOR THE BLAST LAMP

By PAUL J. FOX<sup>1</sup>  
Received July 15, 1914

To the many substitutes for the blast lamp, the writer begs to add one, which, though extremely simple, he has not seen in use in any laboratory that he has visited. It consists of an ordinary assayer's crucible of convenient dimensions, of which the bottom has been ground or sawed off, forming a jacket

<sup>1</sup> Scientist in Soil Laboratory Investigations, Bureau of Soils, U. S. Dept. Agriculture, Washington, D. C.

of truncated conical shape, open at both ends. Thus prepared, the jacket is placed over the crucible or dish to be ignited, with the larger end down. The top is partly closed by a porcelain crucible cover which can be easily adjusted to secure the maximum amount of heat without unduly impeding the draft. Using a Tirrill burner of ordinary laboratory size, it is possible to convert even large amounts of calcium carbonate to the oxide. The crucibles in which the ignitions take place should be covered, but with the lid partly placed to one side to leave a small opening. Besides doing away with the necessity of compressed air, this method of ignition also avoids the strong air current of a blast lamp by which small amounts of light precipitates may be lost. A platinum crucible, also, appears to be less attacked than when a blast lamp is used.

A transparent crystal of calcite was found on analysis to have the following composition:

	Per cent
CaCO <sub>3</sub> .....	99.46
MgCO <sub>3</sub> .....	0.53
Silica.....	0.05
	100.04

This would correspond to a loss on ignition of 44.01 per cent. Two samples of the same material were then ignited, using the jacket as described. Sample No. 1 consisted of 1.0308 g. and after fifteen minutes ignition weighed 0.5779 g., or a loss of 43.95 per cent. Sample No. 2 weighed 1.3117 g. and after ignition for fifteen minutes yielded 0.7355 g. CaO, or a loss of 43.93 per cent. In neither case was there any additional loss on further heating.

A convenient size of assayer's crucible is the Denver Fire Clay No. 9, which measures 3 inches in diameter and 5½ inches high. If a clay ring piece of the same diameter as the assayer's crucible is available, it may be advantageously used as a rest for the triangle that carries the platinum or porcelain crucible containing the sample. This has the effect of extending the jacket below the triangle. The results quoted above, however, were obtained without the use of such a ring piece.

BUREAU OF SOILS, WASHINGTON

## A CONVENIENT FORM OF WEIGHING BURETTE

By H. S. BAILEY

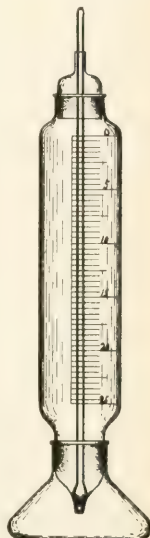
Received August 19, 1914

In making a large number of determinations on various oils the writer at first attempted to use Ripper weighing burettes. He soon found, however, that their weight and especially the necessity for providing some sort of rack for them, when filled, made their use impracticable. As a result of numerous attempts to devise a suitable weighing burette, the one shown in the accompanying illustration, which can be placed directly upon the pan of an ordinary analytical balance, has been finally adopted. Its construction is clearly shown by the drawing in which the three ground joints are indicated by *stippled* areas. The bottom cap serves both as a base to support the burette and as a catch-cup for any leakage. As the sample does not ordinarily come in contact with the two large ground joints, these need not be especially tight when the burette is used for homogeneous non-volatile liquids. The small valve at the tip, which of course must be tight, can be readily made by merely drawing down the end of a glass rod and grinding it into place with a little carborundum and water.

When the burette is used for volatile substances or non-homogeneous mixtures which require frequent agitation, such as milk, a small rubber sleeve is slipped over the top of the stopper and rod, making the joint between them air-tight.

These burettes may, of course, be of any suitable size, the ones commonly used for weighing oil samples having a capacity of about 30 cc. A rough graduation greatly facilitates the weighing out of definite quantities of material for such determinations as the Reichert-Meissl number, in which it is necessary to use approximately the same weight of sample.

FOOD INVESTIGATION LABORATORY, BUREAU OF CHEMISTRY  
DEPARTMENT OF AGRICULTURE, WASHINGTON, D. C.



## SYMPOSIUM ON AMERICAN DYE INDUSTRY

The New York Section of the American Chemical Society devoted its first regular meeting of the 1914-1915 season, on October 9th, at the Chemists' Club, to a discussion of the need and practicability of enlarging the production of dyestuffs in this country. The program was as follows.

Introductory Remarks—Chairman Allen Rogers.

Dyestuffs and the Textile Industry—J. Merritt Matthews, Consulting Chemist to the Textile Industries.

Campaign for American Dyestuff Industry—Arthur Prill, Editor *Daily Trade Record*, Mill Man's Section.

Coal Tar Colors in America—I. F. Stone, President National Aniline and Chemical Co.

Needs of the Textile Industry—Alfred L. Lustig, Chairman of Dyestuff Committee, National Association of Finishers of Cotton Products.

All the papers presented are published in full below. After the reading of the papers, discussions were called for: those by David W. Jayne, of the Barrett Manufacturing Company, Bernhard C. Hesse and I. F. Stone are printed in full herewith.—[EDITOR.]

### INTRODUCTORY

By CHAIRMAN ALLEN ROGERS

At the last meeting of the New York Section of the American Chemical Society, which was held in June of this year, we little dreamed that before another meeting practically the whole of Europe would be involved in the greatest struggle the world has ever known. Many of those who attended that meeting are at present in the ranks of those great armies now engaged in deadly conflict. It is especially sad for us to think that perhaps some of our dearest friends, and members of this society, may be

fighting face to face at this very moment. Just why such a conflict should have been brought about is extremely difficult for many of us to understand. Even as we get the meagre newspaper accounts from day to day we can hardly realize the magnitude of the struggle taking place.

The cause of the European war is a matter with which we are not able to cope, but the effect upon our chemical industries is a topic well worthy of our careful consideration. As chairman of this section, it, therefore, seemed advisable that a conference should be arranged, whereby all sides of the question might be discussed and a more definite understanding of the existing conditions determined.

Although personal feelings and selfish motives may make us more or less prejudiced, we must eventually be influenced by that which seems to be for the best interests of the nation as a whole. What we seek, as chemists, is the *truth*. Let us, therefore, put aside the personal factor and approach the problem with an open mind.

Before entering upon the program of the evening, I should like to ask, for the sake of argument, a few questions which appear to have a vital bearing upon the subject in hand.

1—Is it feasible to manufacture chemicals and dyestuffs in this country?

2—In answering this question should we not take into consideration whether or not we are to seek the American market or the market of the world?

3—Have we a sufficient supply of coal tar to meet the demands of an American coal tar chemical and color industry?

4—If we have the necessary amount of coal tar in this country have we the interlocking chemical industries to make the undertaking a success?

5—If we do not at present have the interlocking chemical industries, is it possible for us to develop the same in face of these well-established industries in European countries?

6—Will it be possible to start with American raw materials and from them build up all-American dyestuffs?

7—Would the manufacture of chemicals and dyestuffs have any influence upon our other export trade?

8—Will it be possible for the European nations to furnish the same quantities of dyestuffs when hostilities have terminated, as they have in the past?

9—Have we a sufficient number of technically trained men to carry on such an industry?

10—What will our universities and technical schools do to train young men for this great industry?

11—What will the Government do to make our patent laws protect American invention?

12—What will the Government do to protect American enterprise?

13—What guarantee will the textile, paper, dry color, leather and other industries give to an American Coal Tar, Chemical and Color Industry?

14—If it is not possible to produce at present all of the great variety of dyestuffs required by these industries, will they guarantee to use such dyestuffs and chemicals as can be made?

15—What support can be expected from the trade and daily papers?

16—Will such an industry meet with financial support?

17—Why is it that we have not in the past manufactured some of the more important chemicals, such as barium chloride, magnesium chloride, oxalic acid, zinc dust and many others?

18—Have we any commercial source of potash?

These are a few of the many questions which must be answered before we can hope to make any headway on the problem. Some of these points will no doubt be covered in the papers of the evening and it is also hoped that those taking part in the discussion will throw some light on the other important questions.

## DYESTUFFS AND TEXTILE INDUSTRY

By J. MERRITT MATTHEWS

That the manufacture of fabrics is an industry dependent to a very large degree on the element of color is a fact which is apparent to almost any one. Textile fabrics are employed in great variety for clothing, for art and utility, as essentials in many lines of industry—in fact, the number of uses for textile fabrics is almost legion. And yet in a great many of these uses color enters as an essential factor in the preparation of the fabric. As color in textile fabrics is obtained by the use of dyestuffs, the latter agents become a very important adjunct to the textile industry.

Although we have come to regard dyestuffs and their colors as highly important factors in the production of fabrics, nevertheless, if we approach the subject from the utilitarian point of view, we find that dyestuffs do not add any real quality to the fabric; the color of a cloth may add much to its artistic appearance and give it beauty and charm that appeal to our esthetic taste, but it cannot be said that the color increases the durability, the strength, or the wearing quality of the fabric. Outside of a certain influence on heat and light rays it is doubtful if color has any real influence on the material value of the fabric; its influence is a purely subjective one. In other words, the practical utility of the fabric is but slightly affected by its color. Our clothes would be of the same practical value to us if they were undyed as if they were dyed; our carpets would wear just as well—in fact better—if they had never been ornamented by the dyer's art.

### IMPORTANCE OF COLOR

Wherein, then, is the value of dyestuffs to the textile industry? In the first place, color is employed in fabrics to satisfy the taste for beauty and the desire for ornamentation. Man from the earliest stages of his existence appears to have had a strong predilection for colors; we find the lowest orders of savage tribes decorating their simple costumes with the varied, though limited, colors at their command. Eve no doubt selected a fig leaf as her costume more from its pleasing shade of green than on account of its utilitarian value as a means of protection against the inclemencies of the weather. It is this innate desire to decorate oneself and the things which one possesses and uses that has led to the wide-spread and almost universal application of dyestuffs in the manufacture of textile fabrics. In the second place, and wholly aside from its artistic value, color is employed in fabrics in order to avoid, or rather to cover up, certain undesirable features. When we wear our clothes for any length of time they become soiled, and the dust and dirt they acquire soon proclaim our intimate associations with Mother Earth. If the fabrics we use were white or undyed, their soiled condition would quickly become apparent in a very disagreeable manner. Consequently, we dye them in suitable colors, and, though they still acquire the same objectionable impurities, these are not visible to the eye, and what we do not see we frequently ignore. I am quite sure that had my present suit of clothes been undyed I should have experienced some hesitancy in appearing before you this evening, but being dyed as they are, I stand here unabashed and thoughtless of their appearance. Our undergarments, our collars, our bed linen, our table linen, our towels, and many other articles of apparel in daily use are now generally left in the undyed condition and even whitened thoroughly by bleaching, in order that when they become soiled they may present a disagreeable appearance and force us to take proper steps towards cleansing them. Have you ever stopped to consider why the blankets in Pullman sleeping cars are dyed a dark grey, why Italians prefer red bandanna handkerchiefs, and why khaki colored shirts are so popular with camping parties? There is food for much thought in these reflections.

In the early days our forefathers naturally employed those coloring matters which were nearest to hand in the decoration



of the fabrics they manufactured. Various colored earths and mineral compounds were used no doubt at first, and then when the tinctorial properties of various plant juices and decoctions became known, these were employed as dyestuffs; all this gradually led to a rather complicated art of the application of dyer's materials. It was found that certain plant juices, though highly colored in themselves, could not be properly fixed in a direct manner upon the textile fibers. But by first treating the fabric with a solution of a suitable metallic or mineral substance, such as alum or copperas or bluestone, pleasing and permanent colors could be produced. This led to a knowledge of the mordant dyes, and this art of dyeing textile fabrics gradually became a highly developed and organized art, and more or less of a chemical science. In fact, the preparation of these vegetable coloring matters and the numerous adjuncts and assisting materials which were employed in their proper application to the fiber, gave rise to important and extensive chemical industries. There were various limitations, however, in the use of these natural dyestuffs. In the first place, the range of color was somewhat narrow, the qualities of fastness were often deficient, there was much variation in the strength and shade of successive lots of dyestuff, the methods of application were often complicated and cumbersome, and it was hard to refine the art of dyeing into an exact science.

#### SYNTHETIC VS. NATURAL DYES

The discovery of America gave a great impetus to the dyeing of textiles by reason of the large number of new dyewoods which were discovered in this hemisphere, especially in the West Indies, and Central and South America. Among these were logwood, which, next to indigo, soon became the most important dyestuff in use; fustic, a yellow wood; cochineal, a very important red coloring matter consisting of the bodies of certain small insects which grow on the leaves of the cactus plant; Brazil wood, also a red dyewood of considerable importance, and many others of minor note.

The great step, however, in the dyeing of textile fabrics, came in the discovery of the synthetic coal tar dyes. This led to an intimate connection between dyeing and chemistry, and in consequence placed the art of dyeing on a more systematic and scientific basis. The discovery of the various coal tar dyes led to the introduction of a wide range of colors, many tones and shades of which were hitherto unknown and unobtainable in dyeing. It also resulted in the introduction of many fast colors, far exceeding the natural dyestuffs in this respect. It gave rise to the possibilities of many new effects and easier, cheaper and simpler processes of dyeing. In fact, the general methods of dyeing soon became standardized to a few definite processes, with the result that the art of dyeing became widely disseminated among the textile mills. It was no longer a secret and mysterious art jealously guarded by the members of its guild, but became an open profession.

It was not long before the coal tar dyes almost entirely replaced the cruder vegetable coloring matters. This was not only due to the fact that the synthetic dyes could be produced cheaper and could be applied more simply and conveniently, but was also because most of the vegetable dyes were of an inferior quality as compared with the coal tar products. In the first place, the vegetable dyes were far from pure coloring matters; they consisted principally of wood extracts, and contained, besides the actual coloring matters, many other extractive substances, such as tannins, sugars, resins, and pectinous bodies of a non-descript character. It was a very costly proceeding to isolate the pure coloring matter from these complex vegetable extracts; in fact, in most cases it was commercially impossible. On this account, the colors given by most vegetable dyes were more or less impure and not clear in tone; they were also liable to be quite variable in different lots of the extracts. In the second place, there are only a few of the vegetable dyes which may be classed

as really fast colors in the modern sense of the term. Indigo was no doubt the fastest color, and still represents the standard for comparison. Logwood, which was once universally employed for the dyeing of black on all classes of fabrics, could be employed for the dyeing of colors fast to washing, but was not especially fast to light and exposure to weather. Before the introduction of the fast coal tar blacks, those of us who are old enough can well remember that our black coats had a tendency to turn to a rusty faded color; this was because logwood was the dyestuff employed. At the present time this defect is very seldom noticed even with the cheaper grades of material, as the alizarine blacks employed for this purpose are eminently fast. Fustic was another much used dyewood for yellow and browns, and this cannot be classed as a fast dye at all; in fact, hardly any of the many yellow and brown vegetable dyes have any remarkable degree of fastness. Among the red colors we had madder and cochineal as the principal representatives. Madder was very fast, being used for the production of the well-known turkey-red; but the coloring matter of madder is alizarine red and in the vegetable extract it is in a rather impure condition, being mixed with other extractive matters, so that when this coloring principle, alizarine red, was prepared synthetically in the pure condition from coal-tar, it very rapidly replaced the crude madder extract. Cochineal was used very largely for the dyeing of scarlets on woolen materials and would be classed as a fairly fast color. The coal tar acid scarlets, which were first introduced, were not as fast as cochineal, and though they were cheaper and easier to apply and displaced cochineal to a very large extent, nevertheless this latter dye held an important position for the dyeing of high class and fast scarlets for a long time. When the anthracene and chrome scarlets, however, were prepared from coal tar, and proved to be even faster than cochineal, this dyestuff gradually fell into disuse. There was also a long list of red dyewoods, but all of these were of inferior fastness as compared with the coal tar dyes and at present are no longer used. Archil and its dried extract, cudbear, were once very extensively employed as the basis of fast purplish red and reddish brown colors on wool and silk materials. It was also used as a bottom color on wool for the dyeing of heavy shades of indigo, giving a rich, deep, and bloomy color. Archil was prepared from the extract of a certain species of parasitical plant growth to be found principally along the sea-coasts of subtropical countries. Enormous quantities of it were once obtained from the western coast of lower California. The coloring matter did not exist ready formed in the plant extract but had to be developed by a series of chemical processes. A large number of fast brown coloring matters, however, have been prepared from coal tar and have almost entirely displaced archil preparations in this country, at least.

#### EASE OF DYEING COTTON WITH SYNTHETIC DYES

As every one knows, the fate of the other vegetable dyes soon overtook indigo, at least as far as its natural source was concerned, and this dyestuff is now almost exclusively made synthetically from coal tar. The introduction of other synthetic dyes of the indigo class and known as the "vat" dyes has greatly raised the quality of dyed cotton materials. The dyeing of cotton with the old vegetable dyes was always a rather difficult matter as compared with the dyeing of wool or silk. This was due to the relatively inert character of the cotton fiber towards the coloring matters, and also to the fact that cotton could not be mordanted with metallic salts with the same readiness as animal fiber; consequently, the processes of dyeing cotton and the colors obtainable were rather limited, which, of course, greatly restricted the use of cotton materials. The discovery of the direct cotton dyes derived from coal tar opened up a new field for cotton dyeing. Though these dyes yielded a very wide range of clear and beautiful shades, they did not possess any great degree of fastness, and consequently could not be employed on cotton fabrics that required much washing and laundering.

This still kept colored cotton goods in a rather restricted and cheap class. The discovery of the fast vat dyes, however, which are eminently adapted to the dyeing of cotton, opened up a new era for the use and manufacture of colored cotton fabrics. With these dyes cotton can be dyed in all manner of beautiful shades, and the colors are as permanent almost as the fiber itself. So remarkably fast are these colors that they withstand the bleaching action of hypochlorites and severe washing and laundering. It is on this account that we can now manufacture colored cotton fabrics for dress goods, shirtings, etc., that will resist the strong chemicals employed in modern laundry methods. It is also possible to adopt many new styles in the manufacture of these fabrics. For instance, cloth may be woven from partly dyed and partly undyed yarns, and then bleached in the piece, the colored yarns not being affected by the bleaching. These improvements in the dyeing of cotton have led to a great development in cotton manufacture, and cotton fabrics are being employed more and more extensively in apparel and other lines of domestic economy.

Dyes, however, are more extensively employed on woolen materials, and the great bulk of the dyestuffs manufactured go into this industry. This condition results from a very simple fact—woolen materials cannot be washed and laundered with the same readiness and impunity as cotton goods. If we washed our woolen clothes, for instance, in the manner we do our cotton ones, they would shrink up and otherwise be sadly injured. Therefore, as I have already pointed out, it is inconvenient to have undyed woolen clothes—they become soiled too easily. Therefore, practically all of our woolen clothing fabrics are dyed, and generally in rather dark colors, and this requires a large quantity of dyestuff. Furthermore, the carpet and rug industry requires an enormous quantity of woolen material, and all of this has to be dyed, for again it is not practical to use undyed carpets.

The woolen industry uses large quantities of the acid dyes and the anthracene and alizarine colors. Indigo is also very extensively used, together with a limited number of the other fast vat dyes. Most of these, however, are not as adaptable to wool as to cotton by reason of the fact that they are employed in strongly alkaline solution, which is not a good thing to use in connection with the wool fiber.

#### GREAT VARIETY OF DYES NEEDED

The textile industry, as you all know, is a very broad one and its products go into almost every other line of industry. Generally speaking, textiles are most often regarded as limited to materials woven for clothing and household and domestic economy. But the term is really much more extensive; for instance, textiles are used for the manufacture of automobile tires, ropes, and cordage, sail-cloth, awnings, window shades, insulating fabrics in electrical apparatus, cloth for bookbinding, and a thousand other uses. The extent to which dyestuffs are employed and the character of these requirements, will, of course, depend on the nature of the textile and the use to which it is to be put. Fabrics used for underwear, for instance, are generally not dyed; cotton hosiery is chiefly dyed black, to a lesser degree brown, and to a very small extent in colors, while silk hosiery is dyed in all manner of colors. It would be foolish to dye fabrics for automobile tires, whereas fabrics for window shades must nearly always be dyed, and with colors of exceptional fastness to light, other qualities of fastness, such as washing, being disregarded as unessential. And so it goes, the wide diversity of fabrics leads to a wide diversity of color requirements both as to shade and fastness. On this account, there must be a wide diversity of dyestuffs to take care of the varied demands of the textile industry, and, in consequence, it has been found impossible to reduce the manufacture of dyestuffs to a few standardized and staple products. In any discussion relating to the establishment of a large American dyestuff industry

this fact must be borne in mind. It must be prepared to take care of the manufacture of relatively small quantities of this, that, and the other dyestuff for some particular purpose and quality of color.

#### MANUFACTURE OF DYES BY THE TEXTILE INDUSTRY

There has been of late a good deal of talk as to the feasibility of the textile industry itself becoming interested directly in the manufacture of dyestuffs and, consequently, I have interviewed numerous textile men on this subject with the view of obtaining a broad opinion of the matter. The general feeling, however, is that the dyestuff industry is entirely separate and distinct from the general textile industry itself; the manufacture of dyes is in reality a highly developed chemical enterprise, and the average textile manufacturer has no more desire to go into the manufacture of dyestuffs than he has of going into the business of mining coal or making steel. The dyestuff manufacturer must be prepared to stand on his own feet and develop his industry through his own energy and capital; he must meet the conditions which confront him (as must every other manufacturer).

When the European war broke out and the regular shipments of dyestuffs were cut off from this country, the textile trade was thrown into a very excited condition. Most of the mills, however, had several months' supply of dyestuffs on hand and this, together with what they have been able to pick up in the market, has kept them going rather satisfactorily up to the present time. There have also been some fresh shipments from Rotterdam to give a further supply to a now practically depleted market. If these shipments can be maintained with more or less regularity during the period of war, there is no doubt but that our textile industries may be maintained without any serious setback. There will, no doubt, be special cases where the necessary suitable dyestuffs cannot be obtained, and this will necessitate a readjustment of styles to a certain extent. If, however, the shipments of dyestuffs from Germany cannot be brought through, or if the manufacture of these dyes is seriously interfered with so that we cannot obtain them at all, then the textile industries here will, of course, be under the necessity of putting undyed goods upon the market. This would be a considerable hardship, for there is no doubt but that the demand for such goods would fall far below the normal, and furthermore satisfactory prices could not be obtained.

#### MEETING PRESENT DEMAND FOR DYES

In this event there are two possibilities to consider: (1) To revive the use of the vegetable dyes to take the place of the German synthetic colors; (2) to manufacture the required dyestuffs in this country. The first alternative does not offer much hope except in a minor way. In the first place, it would require a considerable time to get together the necessary raw dyewoods from the countries in which they grow; then the coloring matters would have to be extracted and properly treated in order to develop a satisfactory strength and quality, and in addition to all this, there would have to be a considerable readjustment of conditions and usages in the dyehouse before the natural coloring matters could be properly utilized to give satisfactory shades. Even then, there would be a great many colors which could not be obtained with these natural dyestuffs, and a great many of our fast colors could not be obtained at all. There are some cases, it is true, where natural dyes would be readily available and could be used as substitutes for some of the coal-tar colors. The output of logwood could, no doubt, be considerably increased in a short time, and this could be utilized for blacks on wool and cotton goods, though fastness of color would, of course, have to be sacrificed. There are large quantities of archil which could also be brought into use on short notice, and this could be employed in many cases with much satisfaction in wool dyeing and carpet dyeing for the production of reds and browns. There is probably



quite a supply of yellow dyewoods which could be made available in a short time. With indigo, however, it is not probable that the production could be much increased for several years, as this requires the careful planting, cultivation and harvesting of crops.

The other alternative open to us is the manufacture of dyestuffs in this country on a scale sufficient to take care of our needs, both with respect to amount and kind of dyestuff. There is already a fair production of dyestuffs in this country, and there is no doubt but what this industry could be satisfactorily developed under proper conditions. It will, however, require time, organized technical effort, and capital, and I am sure we have all three of these commodities in this country, together with the other necessary raw materials for the production of coal-tar colors. But I leave the discussion of this feature of the case to Mr. Stone, who, being a manufacturer of dyestuffs, can tell you all about the possibilities of this industry.

#### PROBLEM TO BE SOLVED BY CHEMISTS

In closing, I would say that the textile industries of this country are very dependent on a proper supply of dyestuffs, and I am sure the textile manufacturers would heartily welcome the firm and permanent establishment of a dyestuff industry in this country, so that we would be self-contained and not dependent on foreign countries. However, they feel that this dyestuff industry must be developed independent of themselves, and while they are willing to give it all legitimate support and opportunity, I doubt if they are at all inclined to grow it as a hot-house product. They believe that the dyestuff industry can be established here based on sound economic principles. The opportunity is here and our chemical manufacturers should lose no time in taking advantage of it. The appeal of the textile industry to the chemist at present is: "We need dyestuffs, so get busy and make them; don't hem and haw, and make excuses, but get right on the job."

50 EAST 41ST ST., NEW YORK CITY

#### CAMPAIGN FOR AMERICAN DYESTUFF INDUSTRY

By ARTHUR PHILL

The technical and commercial aspects of the campaign for an American dyestuff industry are on this program already in better hands than mine, but you may be interested in the publicity features of the movement, for nowadays nothing of moment that effects the general public can be accomplished except by molding public opinion.

You will perhaps permit me to state a fundamental proposition upon which rests the reason for some of the publicity which has been given to the campaign for an American dyestuff industry. A newspaper has two functions, first, to gather, collate and distribute news; secondly, to make men think. The latter of these functions is by far the more difficult to accomplish, but can in a given instance be of the highest value.

The newspaper man has an advantage of position in receiving news at the earliest possible moment. Hence, he is in a position to foresee coming events before the general public or sometimes even before a special industry gets any inkling of such future trend.

Now, if under such circumstances he uses his knowledge to show future possibilities to the paper's readers, he will find unbelievers, well meaning but often short-sighted. Further, if he advocates a change he is certain to arouse the enmity of the old system—hence, the need of a campaign. We ask two far-reaching changes, patent revision and tariff aid. When foreigners obtain Uncle Sam's protection for their brain-work, they should be compelled to use such protective ideas, in part, at least, for the benefit of Uncle Sam's citizens. Again, if we seek American capital to lay out funds for the construction of dyestuff factories, this capital has a right to demand that for-

sign competition be kept out of the country until the whole industry has obtained a firm footing.

In the case of American dyestuffs such a campaign should not really be necessary. A three-fold genius who fully grasped the technical as well as the commercial aspects of the coal-tar situation and who also possessed rhetorical and literary ability to place the matter adequately before all interested, would logically convince them and move them to act.

As no decisive action for the establishment of an American dyestuff industry has as yet been taken, it is evident that this three-sided genius has not yet appeared, but the possibility of united action by such men as compose the *American Chemical Society*—you men here tonight could wage this campaign with certainty of success.

The question which arises in your mind is, Should you take it up and take it up not merely in academic manner, but should you put into this campaign that practical effort and vital force which is essential to victory? The most apparent incentive is the fact that certain branches of the textile trade are today slackening for want of suitable dyestuffs. Not only are mills hampered in production, but human beings are suffering for lack of their usual means of livelihood. Further, every housewife in the land, when she goes into a department store today, finds that her dollar will buy only eighty cents worth, in some cases only fifty cents worth of textiles, as gauged by prices which ruled three months ago. As a result, the household budget of every family in the land suffers more or less.

Another incentive, although little argument need be wasted upon it, is that every country should as far as possible be independent in its industrial activities. America, above all, with her wonderful natural wealth, offers unlimited raw material to the coal-tar dye maker.

But humanitarian and patriotic reasons might not budge you far if a certain other incentive be lacking. The dominating factor in all commercial questions is "Would it pay you to take action?" Here, in the dollars and cents equation, we have the real obstacle to the campaign for an American dyestuff manufacture. It is useless for anyone to cry "American dyes for American textiles," while the majority of persons directly connected with the dyestuff industry get their bread and butter from non-American dyestuff makers and while these persons retain control of the so-called campaign.

I have met many a technical man in the last three months who said: "Yes, we could in from one to two years establish local manufacture of dyestuffs within certain limits perhaps, but sufficient to supply pressing needs. We can do this if we get revision of our patent laws and tariff so as to protect American capital in such venture but—my salary or my retainers come from so and so who do their dyestuff making not far from the Rhine. I can take no action without ruining myself financially. I beg you not to publish a word of this conversation."

The *Daily Trade Record*, having served the textile business for some twenty-two years, also has some good friends among the mill men, to whom we can go in confidence. We recently called the attention of certain of these to an advertisement in a textile journal which ran as follows: "Do not worry about lack of dyestuffs; we herewith assure our customers that we can supply all their needs." The *Daily Trade Record* asked the mill men: "You know this is not true; you yourself have tried to buy dyestuffs from that firm without getting what you were after. Will you back us in our campaign by allowing us to prove the facts by your own business correspondence?" The mill men replied: "If we did, the chances are we would get no dyes at all; this firm would be black-listed by all the importers and practically have to give up business."

Under such conditions, it is evident that the only way to obtain the necessary patent and tariff legislation is to arouse widespread public sentiment among people whose bread and butter



does not depend on the enemies of the movement. You, chemical engineers, if you act as a body, are independent; you could lend the weight of your professional reputation and technical knowledge to prove to the country that we can overcome the technical obstacles. Ten million people in the United States from mill to clothing merchant are dependent on the textile trades and to show these where their bread and butter lies is your problem. Win their votes and you win this campaign. The opponents of American dyestuff manufacturers never mention tariff or patent-revision—they know such proposals would meet with public approval. The foreign makers' agents simply reiterate: "You can not do it."

If you take hold of this subject as a society, show America that we can do it and explain to the other technical organizations in the country how profitable it would be to the United States to develop her coal-tar resources, and through your technical publications and publicity departments obtain the aid of the great American newspaper world, you will certainly succeed in so laying the facts before the American public that the solution we offer will be accepted and appreciated. Home manufacture of dyestuffs is the only solution.

Since a carpenter's union and an iron worker's organization have brains enough to work together for their common good, why could not chemists and civil engineers, even the botanist and the astrologer, possess acumen enough to take united action? Technical workers are the one great intelligent force of civilization, although they hardly seem to understand their strength. In such a campaign as this they could use their strength.

If we do arouse the all powerful public sentiment of the American people, compelling needed legislation at Washington, there will result increased chemical activity not only in dyestuffs, but in all other branches of those numberless industries which are based upon the work of chemists. Your profession will rise to higher and unattained heights in the estimation of the country; financial recompense will similarly multiply as the call for your service increases and future generations will, due to your efforts, worthily call this early twentieth century the "Dawn of American Chemistry."

### COAL TAR COLORS OF AMERICA

By I. F. STONE

MR. CHAIRMAN AND GENTLEMEN:

It gives me great pleasure to be able to appear before you this evening, to clear up, if I can, the general skepticism which seems to exist in connection with the manufacture of coal tar dyes in the United States.

#### DYE INDUSTRY IN THE U. S. FOR 30 YEARS

That there is such an industry in the United States is a fact and has been for over thirty years. That we cannot compare with Germany in magnitude is of course true, and that we shall be able to increase our production in the near future to take over all of the colors now supplied by Germany is also manifestly impossible, but that it is possible to increase the American production very materially is a fact, depending on certain conditions of which I shall speak later. That there has been more or less prejudice against dyes made in America is also true, and these dyes are fully as good as any made in Europe, although it has been a struggle to prove that the latter statement is absolutely true. Even at this late day there are people who would always give the preference to European dyes at the same price and quality, if they had an opportunity to do so, and they are abetted in their belief very naturally by the European representatives.

Only a few days ago, among other letters we have received asking about the manufacture of dyes in this country, was one from a very substantial trade journal which circulates largely among the textile mills. Among other things it says: "No one believes that the American dyestuff manufacturer can com-

pete with the German. The Germans are counted wizards in dyestuff chemistry and I doubt if you could interest a great number of manufacturers in a domestic product at the same price as quoted on exactly the same thing from Germany." After a couple of pages of such argument it finally suggests that we take up the matter of advertising with them to change the sentiment of the buyers, which is very naive to say the least.

But the point is, if a journal with the influence of this one should express such sentiments among its subscribers, how unfair it would be to the American manufacturers of dyes, and it is simply an instance of one of the small things against which we are struggling. On the other hand, in the past few weeks we are encouraged by numerous letters from actual consumers of dyes, among them some of the largest textile mills in the country, complimenting us upon the way we have been handling our products during the present abnormal conditions, and advising us that they would in the future give their preference to American colors whenever we are able to offer them in competition with foreign colors; *i. e.*, when we can supply them with the quantity of colors consumed, which hitherto we have not been able to do by reason of not having a production sufficiently large to take care of all the trade. So life does have its compensations and the American dyestuff industry from now on starts out on an equal footing with the German industry, as far as the good-will of the consumers is concerned. It is therefore only a question of being able to produce a large enough quantity at competitive prices to insure a large proportion of the business of the United States for the American manufacturers.

Barely two months ago a comparatively small percentage of the population of the United States knew anything about aniline dyes or dyestuffs, those who did know something being mainly connected with industries which used these products. Even those who did use them had only a vague idea, as a rule, what they were and their source, except in a general way, that they were made from coal tar and that Europe was the principal source of supply. They were even regarded by a large percentage of the consumers as a mere detail of their business, and were put in among the sundries with such items as oil, soap, and I might almost say paper, string, and such miscellaneous supplies, notwithstanding that it requires the highest order of scientific training to produce these colors and a long experience and knowledge of them in order to sell them successfully. The average dyestuff salesman was received only with tolerance and usually referred to some minor employee for his interview. Suddenly something happened. A great war was declared, and the great source of supply was one of the principal nations involved. Some buyer, more intelligent than the ordinary one, discerned that the stock of dyestuffs would be more or less limited if not entirely cut off under these conditions, and immediately made attempts to secure a good supply for his future wants. The news soon spread among others until there was a general scramble for dyestuffs and men who ordinarily gave the matter very little attention are now looking after it personally, and interviewing and corresponding with the heads of such firms as they think can accommodate them. The newspapers took up the matter and published columns of more or less accurate information as to the situation. The general public was therefore given an idea of what was going on, and now know more of the source and supply of aniline products than they ever knew before.

The unfortunate conditions now prevailing have at least been of some good in demonstrating to our people that they should be as independent as possible of other nations in connection with their supply of such products as are needed in this country, and there is now a general demand that the production of aniline dyes as one item should be immediately developed to such an extent that we may be independent of all other nations.

The serious question now therefore is whether or not such an industry can be developed to such an extent, and this question can be answered only by some extended and more or less superficial explanation of conditions. It is not my intention to put before you a scientific or technical paper on the subject, as most of you are more or less familiar with the general conditions surrounding the manufacture of these products, or at least can easily read up the details. I do wish to give you, however, a practical statement of the facts so that you may see why the industry has not developed in this country as it has in Europe, more particularly in Germany, for other nations are no further advanced than are the United States.

#### RAW MATERIALS FOR DYES

Aniline is a product of coal tar, that is, coal tar is the primary raw material from which colors are produced, and it was obtained originally in the manufacture of coal gas; but recently the coke ovens used for making hard coke have furnished a large and constantly increasing quantity.

The first distillates are such products as benzole, toluole, xylole, phenol (carbolic acid), naphthalene, anthracene, etc., and these are produced largely in the United States as well as in Germany; benzole, for instance, which is probably the most important of the group, is not only the base for the manufacture of the intermediate products of aniline dyes, but is also used largely as a solvent in place of benzine and gasoline, and in fact, in Europe is largely used as a fuel for automobiles as a substitute for the same products. The prices at which it sells in this country are practically the same as in Europe, as are also the prices of the other distillates first mentioned. Up to now, the supply has kept pace with the demand, and there is no overproduction, but if the manufacture of dyes is to be considerably extended it will then be also necessary to extend the production of benzole which can be done in the course of time by substituting by-product coke ovens for those that do not at present recover their benzole. This, however, hinges on the ability to make a profit on this recovery, so that there is a chance that the price of benzole may increase to some extent.

Another base of importance is naphthalene, which is made largely because there is a great demand for it, the consumption in the United States being upwards of nine or ten million pounds, not alone for the manufacture of dyes but more as a moth preventive. Of the quantity consumed here about one-third is produced in the United States while the balance comes about equally from Germany and England.

It is evident, therefore, that the United States starts out on an even basis with Europe as far as the supply of the first raw materials is concerned, and that the natural resources of this country are available for an increase in the products which are manufactured from this source. So, in the beginning, we are as well placed for raw material here as they are in Germany; in other words, this is not a hot-house industry as some people have claimed, but is a part of the natural resources of the United States.

From these distillates are manufactured what we call intermediate products such as nitro-benzole, aniline oil, aniline salts, toluidine, xyloidine, cumidine, benzidine, binitro-benzole, nitro-benzole, sulfo-acids, and a host of others.

#### INTERMEDIATE PRODUCTS LACKING

It is here that the first check in the economical manufacture of aniline dyes is encountered, for the reason that with one or two exceptions, which I will mention later, none of these intermediate products are manufactured in the United States because up to now there has not been a large enough demand for them to make their manufacture economically possible. On the other hand, Europe—Germany particularly—has so developed the demand for these intermediate products that many plants have been established for their manufacture, most of

them specializing on certain compounds, so that in the aggregate they are all produced on the most economical basis. Up to within recent years, few of the aniline dye manufacturers made these products themselves, but depended largely on the aforementioned so-called specializing factories for their supplies; this is now changing, and some of the large color manufacturers are now making the principal intermediate products themselves, although none of them make everything which they use. It is then very necessary, if the United States is to be independent of Germany, that these intermediate products be manufactured on a large scale in this country, and it is here that we ask the Government to start in with a sufficient protective duty to allow the business to be developed. The present duty of 10 per cent, which was put on only in the last tariff bill, is not really sufficient for the purpose. As the group was duty-free previously, there was no incentive to begin their manufacture here.

#### ANILINE OIL

One exception which is made here is aniline oil, the manufacture of which was commenced about three years ago. The quantity now produced is about one-quarter and perhaps more of the total consumption of the United States, taking oil and salts as one product. The quality is very satisfactory as compared with the German and English products, and has been used by our own factory in the manufacture of aniline dyes since the beginning; in fact, if it were not being produced in this country at the present time the American dye manufacturers would not be able to continue to run as they would be unable to obtain supplies from Europe. As a result, manufacturers here are able to relieve the scarcity of aniline dyes, and have thus been of great benefit to American consumers. They will be a great factor in this relief as long as these unfortunate war conditions continue, so illustrating the great benefit to the people at large in having this class of products manufactured here, entirely independent of Europe.

Unfortunately, however, the commercial side of the manufacture of aniline oil has not been so satisfactory. In the beginning the manufacturers had no protection in the way of duty and were compelled to compete on an even basis with Europe, which could not be done successfully. They did, however, succeed in securing a duty of 10 per cent under the present tariff, which went into effect in October, 1913, but unfortunately this did not avail them anything in the beginning because the convention which controls the production of aniline oil in Europe immediately reduced their prices 10 per cent to offset our duty, so that we were no better off than before. This is a sample of what is called unfair competition on the part of European firms in their attempt to prevent the increase of the aniline industry in this country, but it could be readily checked if our Government would incorporate in their tariff what is known as the "dumping" clause, which would forbid the importation into and the selling in the United States of any product at a less price than it is sold in the country where it is produced. In spite of this check, however, the American manufacturers will continue the manufacture of oil, hoping that conditions will change in the near future so that they may be able to work at a profit. When this object is attained their plans are then to take up the manufacture of other intermediate products, until everything necessary is finally manufactured here. As a matter of further interest, I might say that our own factory in Buffalo made aniline oil thirty years ago, but we were obliged to give up its manufacture at that time owing to inability to secure benzole, which situation is, however, now changed, as it should be possible to obtain sufficient benzole to continue the manufacture under advantageous conditions.

#### NITRO-BENZOLE AND CARBOLIC ACID

The other exception to my statement that these intermediate products are not manufactured here is nitro-benzole, known also

as crude oil of myrbane, which is in some demand from outside industries as well as the aniline industry, but not to so large an extent as aniline oil, and which is made here from time to time as conditions warrant; *i. e.*, when it can be made at a profit in competition with Europe.

There is another demand springing up for these intermediate products, which may increase their consumption to such an extent that there will be a large demand entirely outside of the aniline industry, *e. g.*, in the manufacture of smokeless powder and other explosives, the makers of which are now using such products as diphenylamine, tri-nitro-toluole, nitro-benzole, pyridine, nitro-naphthaline, etc. This will finally create a demand which will necessitate their manufacture in this country as a matter of safety, for if the Government depends on explosives made from these materials, it will in self-defense have to create some sort of subsidy or tariff protection, making it possible for their manufacture irrespective of European competition. This is also true of carboic acid, which is a primary coal tar product and which is used in the manufacture of picric acid, and explosives used by the Government. Carboic acid not being manufactured here at present to any extent, is now practically unobtainable from Germany or England since they have placed an embargo on this product.

#### NUMBER OF DYES MADE IN UNITED STATES

From these so-called intermediate products we then come to the manufacture of the actual aniline dye as sold in commerce, and their number is voluminous and complex. My good friend, Dr. Hesse, for instance, recently stated in a published lecture that there were some nine hundred different manufactured products, most of them as different each from the other as a pair of shoes is from a pair of socks. Of these nine hundred he observed that some seventy-six are now made in this country, but that this number is apparently not sufficient to meet the users' demand, in which statement I am quite ready to agree with him, except that we now make nearly one hundred types, which is more than he gives us credit for making. I will say, however, that of these nine hundred original types a great many are obsolete and probably we could get along quite well with a much less number, but as the one hundred made in America are all live types and those which can be manufactured regularly, you will see we are making really a much larger percentage of the total than is apparent at first glance. I might also venture the statement that with the hundred or so types already manufactured here together with perhaps a few more which we would be prepared to take up on short notice, we would be able to furnish the American consumers perhaps ninety per cent of their color demands (speaking now of types or shades and not of quantity), the other ten per cent, which we could not furnish, being such products as alizarines, indigo and patented specialties requiring large installations which it would take a long time to complete.

It would perhaps be interesting in connection with these colors to give a hasty sketch of their beginning and development into the great chemical industry of Germany, with its investment of millions of dollars and employment of thousands of people.

#### HISTORY OF DYE INDUSTRY

The first color discovered was mauve, a sort of violet, by Perkin in 1856; then followed magenta and fuchsine in the same year, and a small establishment for the manufacture of the same in England, which was not, however, very successful. In 1862 came the discovery of Soluble or Water Blues, then Hoffman's Violet about 1863, Bismarck Brown in 1863, Naphthol or Martius Yellow in 1864, and the Nigrosines in 1867.

It was about this period that the Germans became actively interested in these products, and commenced their patient, intelligent, and careful researches into the subject, which later

resulted in most wonderful discoveries and the development of this industry in their country.

Then followed the discovery of Orange, Fast Red, Chrysoidine, Malachite Green, Ponceau (Scarlet), Methylene Blue, Eosines, and Metanil Yellow about the years 1875, 1876, 1877 and 1878, and the manufacture then became one of recognized merit and importance.

After 1880 followed in rapid succession the discoveries of Auramine in 1883, Tartrazine in 1884, Benzo Purpurine in 1884, Congo Red in 1885, Benzo Azurine in 1885, Naphthol Black in 1885, Diamine Red in 1886, Rhodamine in 1887, to mention only a few of the best known and most successful colors.

From 1880 to 1890 might be called the golden period of the business. Just prior to that time alizarine had been discovered, red in 1871, blue in 1877, patented, and successfully produced and sold at high prices with correspondingly large profits. It was about that time that our German friends discovered the advantage of securing an exclusive market in the United States through their patents which enables them to sell at high prices here, although continuing the manufacture in Germany. The profits were enormous from such patented products as alizarine, benzo-purpurine, diamine red and other direct dyeing cotton colors, Auramine, Rhodamine, Tartrazine, and other such colors, which were discovered and put on the market in that period, and put the German industry immediately on such a high pinnacle of success that it has continued until the present time.

In the nineties came the discovery of such important products as direct blacks for cotton, and acid and chrome blacks for wool, the total consumption of these blacks being much larger than all the other colors combined.

Also at this same period began the first of the patents on synthetic indigo, of which there are many. It was finally put on the market at a tremendous expenditure, and has been a commercial success only in the past few years, though it has now practically replaced the natural indigo.

I might say in connection with the development of colors, that in the nineties came also the development of such pharmaceutical products as phenacetine, antipyrin, etc., which paid enormous profits to the manufacturers and which were also controlled by patents.

#### GERMAN INVESTMENTS IN DYE INDUSTRY

Such, then, is the wonderful development of the coal tar industry, there being invested at this time in Germany something like \$400,000,000, probably more, employing some 50,000 people. Some of the factories pay dividends of 25 to 30 per cent, after charging off a third of their profits to sinking funds for the erection of new plants and for other such purposes. This latter has been done for so long a period that most of the present property and plants do not appear on the books at all as assets, but have been built from the surplus profits. This statement is made on the basis of a balance sheet for 1913 issued by one of the great factories, which has a capital of 55,000,000 Marks, but whose stock is selling for over six times par value, showing that the actual capital in the business was at least four times the shares issued, or some 200,000,000 Marks. On a capitalization of 55,000,000 Marks they showed a profit of 25,000,000, or nearly 50 per cent, one-third of which was written off from their real estate and plant account, leaving about 16,000,000 Marks from which they paid a dividend of 28 per cent. Assuming that I am correct in my estimate of some \$400,000,000 being invested in the industry in Germany and assuming that a fair proportion of their production is shipped to the United States, it would mean that if the United States were to develop this industry to take care of all their consumption here, they would need millions of dollars and would need to employ thousands of people, which will give you an idea of the magnitude



of the business that it is now proposed that we establish here to its full extent.

#### VALUE OF DYES IMPORTED

It might be interesting at this point to give you the value of the aniline products imported into the United States from these European factories, the figures being for 1913: Aniline dyes, about \$7,000,000; indigo, \$1,000,000; alizarines, \$1,500,000; a total of about \$9,500,000, these figures being, however, cost prices. When the American duty of 30 per cent is added on aniline dyes, and further amounts added for expenses and profits on their sale here, it means that the American consumers are really paying something like \$12,000,000 for their supplies, not counting the colors produced in America, which may perhaps reach about \$2,000,000, the production in America being some 15 to 20 per cent of the total consumption. These figures do not include the importation of pharmaceutical products which are made from coal tar and which is in itself a large business.

Our German friends are entitled to all the benefits which have accrued to them by reason of their shrewd, intelligent, and careful attention to this industry, but with such a statement as the above, does it not seem as if they had had enough and that it is now time for the United States to participate in this great industry when they are so well prepared to do so by having as good, if not better, natural resources than has Germany, and being consumers of so large a proportion of the German products? We must admit at once, however, that the United States cannot compete with the German manufacturers under normal conditions, first, because they have a great advantage in capital, experience, and the general advantages of everything that goes with a successful and enormous business; and second, because the actual expenses of producing in Germany through labor conditions, and so forth, are much less in this country, so that some way must be devised to put the United States on a competing basis. Two things, are necessary for this.

#### NEED OF PROTECTIVE TARIFF

First, a sufficient protective tariff, which does not necessarily mean, by the way, an increased price to consumers, although many people seem to think so. For instance, the *Scientific American* of September 26th falls into this common error: it states that with an average importation of about \$6,000,000 worth of coal tar dyes in the last thirty years we have a total importation of \$180,000,000 during that period, and assumes that had duties been 10 per cent higher it would have meant that a total of \$18,000,000 would have been paid as an insurance premium against the possible event of a war such as is now disturbing commerce. Even if the *Scientific American* were correct in the statement that \$18,000,000 would have been paid as an insurance premium in thirty years, this really would be cheap insurance compared with the enormous value of the colored goods manufactured, assuming that the goods could not have been manufactured without the colors, which is almost the situation as it stands to-day if colors are not soon obtained in the necessary quantities. When I speak of goods in which aniline dyes are used, I mean the whole range including textiles, leather, paper, silk, paints, and the hundred and one other dyed manufactured products.

In my opinion, however, based on experience, just the contrary to the *Scientific American* opinion is true, for the reason that a higher tariff would have stimulated production and competition, and competition always controls the price. This is shown clearly by actual facts; e. g., on indigo and alizarine colors there is no duty, and as a consequence they are not made here. Theoretically, therefore, they should be sold very cheap, but as a matter of fact, by reason of no competition here, they are controlled by conventions in Europe which make a uniform price so that consumers are unquestionably paying more than if such products were made here in competition. On the other

hand, take for instance direct cotton black, an aniline dye which has a protective duty of 30 per cent; it is made in this country in large quantities and the Europeans have been obliged to reduce their selling price in this country to less than that in Europe, so that American consumers are enjoying prices as low as 17 to 18 cents for a color which sells at from 22 cents and upwards in Europe under normal conditions.

Does any one believe that the low prices would have been made in this country were it not for the competition here, and does it not therefore prove that competition here regulates the price and that it is not so much a question of duty? The American manufacturers do not want such a high duty, but they do want enough to equalize the difference in manufacturing conditions between this country and Europe and they want protection against the "unfair competition" referred to in my remarks in connection with aniline oil; in other words, the inclusion of the so-called "dumping" clause, and with a proper tariff on these lines the business could be successfully developed. If we could get our intermediate materials at the prices paid by the Germans, and then secure for our colors the prices obtained by the Germans for finished colors in other countries, plus the actual American duty, the problem would be solved, for this actual American duty, if sufficient, would cover our extra cost of manufacturing and put us in the exact position of the Germans as far as our selling prices are concerned.

#### NEED OF CHANGE IN PATENT LAWS

Second, our patent laws must be modified, so as to require the manufacture in the United States of all those articles for which U. S. patents are issued. England has within the past few years made such changes in her patent laws, and Germany has always required the manufacture of patented products in her own country. Her present law reads in general that the owner of a patent must work the invention to an adequate extent in Germany or at all events do all that is necessary to secure such working, and if not, then if the public interest is such that the granting of permission to others to use the invention appears needful, that is done by making some arrangement with the owner of the patent so that he receives adequate compensation—but the manufacture of the product itself is insured for Germany. About 1909 a similar clause was threatened in the patent laws of this country, and to head off such action Germany negotiated a treaty with the United States by which the German working clause was made inoperative on American inventions; in other words, in return for the United States allowing Germany to continue to manufacture her products in Germany and export them to the United States, the United States was allowed a similar latitude in exporting her patented products into Germany, but whether or not the financial results of this treaty were beneficial to the United States is a question; it certainly did not work out to the benefit of the United States as far as coal tar products are concerned.

In what I have already termed the golden period of the industry, there was from 1880 to 1883 a duty of 35 per cent *ad valorem* and 50 cents per lb. specific, which gave ample protection to the industry. As a consequence there were nine or ten factories in the United States, and the prospect of becoming independent of other nations for our supply of the aniline products was bright indeed, but the tariff act of July 1, 1883 abolished the specific duty of 50 cents per lb., leaving only the *ad valorem* duty of 35 per cent, and fixed a 20 per cent duty on the intermediate products, which left only a net protection of 15 per cent and immediately checked the industry here. No new factories were started, and within one year after the new tariff took effect five of those already established were forced out of business, leaving only four to continue the work. Those four would have gladly followed their example, but as they had invested large sums of money in plants which would be an entire loss if abandoned, they decided to continue to operate their

factories, hoping for more favorable legislation in the future. Thus far they have been bitterly disappointed, and no tariff since that time has given them sufficient protection to develop their business to any large extent. Of course a specific duty of 50 cents in those days was not abnormal as the selling prices of the colors were so much higher than at present, and if a proper duty had been continued it would have had the same beneficial effect, but the abandonment of a sufficient duty has left open the admission of colors on a basis which really gives no protection at all.

In addition to the protective question as a stimulant to the creation of the dye industry in America, if the Government had in the eighties required the manufacture in this country of all products for which they issued patents, then it would have at once created a large industry here, for the European patentees would have been forced to build branch factories in the U. S. These factories would undoubtedly have developed other products even though they had originally been erected only for the manufacture of patented articles, and while this would not have helped the then American factories it would at the same time have inevitably created a large industry with beneficial results to the country at large.

As I have stated, there are now four factories in the United States manufacturing aniline dyes, our own factory having been established in 1879. While of slow development, it has been successful to the extent that it has kept in business and now manufactures practically all of the seventy-six different colors mentioned by Dr. Hesse, or to be correct, the one hundred, to which I referred in the beginning of my remarks, these colors being all of the original colors such as Bismarck Brown, Magenta, Chrysoidine, Fast Red, Water or Soluble Blues, Eosines, Nigrosines, a comprehensive line of direct dyeing cotton colors, and a comprehensive line of acid and chrome colors for wool and silk. The list could easily be extended to the manufacture of practically all of the necessary colors now demanded and not covered by patents, thus giving the consumer a large variety and insuring practical independence of Europe under any conditions. The resulting business would be large, except in comparison with the great German industries, which stand alone in their magnitude.

#### PRESENT WORK OF AMERICAN PLANTS

All of the American factories will continue to manufacture colors to the best of their ability, but they cannot promise any extensive increase in their production without the support of the Government in the line of tariff protection, and incidentally, the change in the patent laws. The latter, however, are not now quite so important as to colors because many of the original patents have expired and we are free to manufacture a large line of colors provided it is made commercially possible for us to do so, we having already demonstrated our ability as far as experience and willingness are concerned. I might mention that our own factory in Buffalo, known as the "Schoellkopf Aniline Works," was the pioneer in the manufacture of such products as nitro-benzole, nitro-toluole, binitro-toluole, binitro-benzole, aniline oil, aniline salts, dimethylaniline, and quite a range of sulfo-acids, some of them of our own invention, which are necessary for the manufacture of both acid and direct colors. We have also made such products as pure carbolic acid and pure naphthalene, but were obliged to give them up as well as the others because we could not compete with the European manufacturers; we are now hoping that they can be taken up again either by us or by possible manufacturers of intermediate products and their manufacture continued successfully in this country. Under the present abnormal conditions our factory is again making some of these products in order to keep in operation, since it is not a question of price but of ability to manufacture aniline dyes at almost any cost, such is the demand. But whenever conditions be-

come more normal we shall necessarily have to give up the manufacture of these intermediate products for the same reason that we had to give them up before, *viz.*, that we can purchase them in Europe for less than we can manufacture them here.

I might mention further that our factories in Buffalo are still controlled and directed by Mr. J. F. Schoellkopf, who originally established them, being assisted a little later by his brother, Mr. C. P. Hugo Schoellkopf, so that they have had nearly thirty-five years of continuous experience in the manufacture of aniline products, and are fully competent to continue the manufacture in a large way, should favorable conditions develop.

This paper is not intended to appeal for sympathy or help from the Government or from American consumers because we happen to be so placed for the past few years that we could not develop our business as it might have been developed under different conditions, and the American factories even as they are, are prosperous and quite able to take care of themselves up to a certain point; but it is intended to show that the business cannot be extended to large proportions for the protection of American consumers, except with Government help as to tariff and patent laws, and with the assistance of the consumers themselves, which means giving the American manufacturers the preference wherever possible and assisting them to secure the necessary help from the Government.

Here then is a superficial history of the progress of the aniline industry from its inception to the present time, not only in this country but in Europe, and the situation as related to the present and future manufacture of these products in the United States is fully explained. Will the United States Government continue its indifferent policy of practically allowing this important industry to drift along as heretofore, or will it now wake up and seize the opportunity to make itself independent of all other nations in its supply of coal tar products not only for aniline dyes for commercial purposes, but for pharmaceutical products, which relieve illness and pertain to the health of its inhabitants, and for products for the manufacture of explosives which would be absolutely vital in case of war? The future alone can answer these questions.

#### ADDENDUM

After reading this paper, in reply to a question as to whether or not any original work had been done by the American dye manufacturers, that is, had they discovered any new products, Mr. Stone stated that sixteen patents had been taken out by the Schoellkopf Works between 1884 and 1903, comprising colors and intermediate products. One of these products, known as Schoellkopf Acid, had been taken up by one of the largest German manufacturers and used extensively by them; another product, Direct Black, had been taken up by another large German factory and also made extensively by them. Both products were used, of course, through arrangements with the Schoellkopf Works.

#### NEEDS OF THE TEXTILE INDUSTRY

By ALFRED L. LUSTIG

MR. CHAIRMAN, MEMBERS AND GUESTS OF THE AMERICAN CHEMICAL SOCIETY:

I have been asked to say a few words to you on the needs of the textile industry and, as Chairman of the Dyestuff Committee of the National Association of Finishers of Cotton Fabrics, I am glad to have an opportunity to bring our needs to your attention. I would at this point like to state, however, that I am confining my remarks to the situation as it affects the dyer and printer of cotton fabrics (the branch of the industry with which I am most familiar), although I believe that the wool and silk trades are in a condition similar to our own.

As you all know, a very large proportion of the colors used by textile finishers are imported from Europe, mostly from

Germany. Owing to the war, our regular sources of supply are considerably disturbed and many of us question whether, later on, it will be possible to obtain quantities sufficient to keep us going.

When the European War broke out two months ago, two problems presented themselves to the users of coal tar colors:

I—How to secure the necessary colors and supplies to keep our plants going during the war and during the period of reconstruction following the war.

II—Realizing how dependent we have been up till now on the European makers for our supplies of coal tar colors, what steps could be taken to prevent a repetition of the present conditions in the future?

In our desire to secure the necessary supplies to keep our plants going, we undoubtedly tried to get all we could from the importers, who met the unprecedented rush of orders by apportioning the available supplies pro rata and dividing additional importations so as to keep all of us working as far as it was possible.

There has been a good deal of discussion and comment as to the ability of the importers to keep us supplied under present conditions, and there is a grave doubt in my mind whether on some special lines of colors it will be possible to meet our requirements during the next few months. But, on the other hand, I feel that everything possible is being done to facilitate importations and to secure such supplies as can be obtained in Europe, and I believe we shall continue to obtain some colors, at least for a while, unless conditions should unexpectedly change for the worse.

We have had to pay somewhat higher prices and will probably have to pay still more later on. Unfortunately, we have not been able to obtain a proportionate increase for our work in many cases, but we believe that this problem will adjust itself as soon as our present agreements, which, in most cases, were made before the first of August, are completed.

We must acknowledge the unremitting efforts made by the importers of dyestuffs and the exceptional energy, fairness and ability, with which they have handled the situation. Speaking from my own experience, I find that they showed the greatest patience under very trying conditions and worked day and night to meet the emergency.

In order to preserve the stock of colors and supplies, we have asked our customers to cooperate with us and, with their aid, we have been enabled to accomplish a good deal in preserving our color stocks.

Some of us, no doubt, grasped the opportunity to check all unnecessary waste in our own plants, which undoubtedly has also helped the situation materially.

Some of us have proceeded to replace imported coal tar colors with products of domestic manufacture. This is true to a limited extent in the use of various dyewood extracts in place of alizarines and in some cases pigments have been substituted for vat colors in printing shirting fabrics. Many experiments are being made in dye houses, trying out methods which would enable the dyer to use dyewoods and other available materials for some shades, where in the recent past coal tar colors have been used.

There is also a tendency on the part of the designers to adapt themselves to the present conditions by developing styles that can be executed without the use of coal tar colors. I refer to the strong tendency for black and white effects in printing, which can be produced with logwood; also the probability of a strongly increased demand for white goods. With all these attempts to preserve our stock of coal tar colors, with a few cases of possible substitutions and the changes of style, we are still confronted by the fact that most of us have supplies to last us for a short time only. If importations cease for any considerable length of time, we shall be obliged to curtail production and later on, in many cases, shut our plants down completely.

Having shown you the immediate effect of the conditions brought about by the European war on our industry, I shall now take up the second problem: What steps can be taken to prevent a repetition of the present conditions in the future? There seems to be only one answer to this—encourage the development of the coal tar color industry in this country.

We all know that a limited number of these products have been made here for a number of years, but we are under the impression that so far the industry has not been in a very flourishing condition. The first step, the tar distillation, had not been worked out successfully until within the last few years and our color manufacturers have depended on Europe almost exclusively for the intermediate products required to produce the finished article.

Their profit was in the possible margin between the duty on intermediate products and the duty on the finished colors, minus the cost of manufacture. I have heard it stated that this margin is not sufficient to encourage capital to embark in this branch of industry.

The next step would seem to be an increase in the duty on intermediate products and an increased margin between the duty on intermediate products and the duty on finished colors. Owing to the possibility of a change in tariff after every national election, there could be no absolute dependence on the conditions established through this method.

Then, there is a question of patents to be considered and, though hundreds of these have expired, the industry is progressing continuously and patents on a great many of the most desirable products are undoubtedly still in force. I believe, however, that with sufficient encouragement, the industry would soon attract the attention of the chemists of this country and that our research laboratories would develop new products quite as they are being worked out in Europe at the present time.

There are several ways in which the textile manufacturer can help the development of this industry. Under all ordinary methods of competition, the manufacturer will buy his products at the lowest price. It is quite conceivable that if the manufacture of certain products is taken up by domestic plants it might be necessary to pay temporarily a little higher price for the domestic article, in order to allow the development and smoothing out of these particular processes; but, later on, after the manufacture of these products is thoroughly developed, I feel that domestic competition and increased efficiency will tend to lower the prices. This has been proven in the products which are being produced in this country on a large scale and which, I am told, are meeting foreign competition quite successfully.

The textile finisher would have to sacrifice temporarily in some directions, in order to accomplish the greatest good for all, which would be a gradual development of the coal tar industry in the United States. Most of the colors which we use in our processes, representing as they do in many cases the highest development of synthetic chemistry, would be among the very last ones to be manufactured here. And yet I, for one, feel that it would be good business judgment on our part to bear additional financial burdens for some years to come, in order to help to establish an American coal tar industry, and in this way ultimately benefit ourselves.

I understand that the coal tar color manufacturers of Germany have in the past given this matter some consideration and, while I am convinced that we have the ability and energy to develop the industry, I believe that by cooperation between the German color manufacturers and those interested in developing the industry here we could gain years of time, save large sums of money and could establish the industry under the most favorable conditions.

The German people will require all their financial resources to repair the damages caused by the present war; but they can



furnish us with patent licenses and with some experts, which would form a nucleus for the elaborate steps needed to work out this problem. I believe that by the resulting coöperation with the European manufacturers who, at the proper moment, might be induced to enter this field, we could help to establish the industry here and in this manner prevent a recurrence of the conditions which jeopardize textile interests at the present time. This might be done irrespective of material changes in our laws, such as, the amendment of patent laws, changes of tariff, etc., which are already being given serious consideration.

I have not attempted to illustrate the importance of textile industry by statistics. The value of the coal tar colors used is only a fraction of the value of the finished textiles and the percentage of the coal tar colors used in our industry is only a fraction of the total amount of coal tar derivatives used in this country in various lines of activity. But, I believe that the same argument, which I have tried to apply to our industry, could be successfully extended to the dyeing and finishing of other textiles and in a general way could be further applied to other industries using coal tar derivatives.

THE APPONAUG COMPANY  
APPONAUG, R. I.

## THE POSITION OF THE AMERICAN TAR DISTILLER

By D. W. JAYNE

Dr. Rogers asked me to respond to the question "Why doesn't the American tar distiller work up his coal tar products or sell them for the manufacture of dyestuffs?" in this discussion, and referred to the paper presented before the Berlin Congress, in 1903, by my father. I want to quote the opening paragraphs of that paper:

"The coal-tar industry, especially the manufacture of the more refined products, has not reached in the United States that degree of development which characterizes the industry of Europe, and which should be commensurate with the wealth and population of the country.

"The chief reason for this backward condition has been the scarcity of the raw material, the coal tar itself, due to the very general use of petroleum and electricity for illumination, and also to the large production of oil and water gas."

In the decade since this was written conditions have changed so that today it is no longer a question of the raw materials.

This subject now divides itself into two parts, under each of which the tar distiller must take into account two considerations:

I—Why doesn't the tar distiller work up his products to sell to others for the manufacture of dyestuffs?

1—Can he get a better return in dollars and cents for the separated products than for the straight distillates?

2—Has he a real demand for specific separated products by manufacturers of dyestuffs, which will assure him a constant outlet for the products if plants are erected for their recovery?

II—Why doesn't the tar distiller work up his products and manufacture the dyestuffs himself?

1—Must he find outlets for excess material now produced or to be produced?

2—Does he believe that a complete industry when established would be profitable, and is he willing to operate at no return and to invest millions based on the belief of ultimate success?

You will understand at once that all of these considerations are purely commercial ones.

Let us first realize that there are four crude coal-tar products which constitute the bulk of the material used in dye manufacture: namely, benzol, naphthalene, anthracene and phenol. Of these, but naphthalene and anthracene concern the distiller of tar, as neither benzol nor phenol occur in American tars in sufficient amount to be considered a factor by the tar distiller. Benzol and its homologues have been refined for years and available to anyone considering the manufacture of intermediate products: phenol would have to be made synthetically from benzol

to obtain sufficient quantities, so that we can pass over these two basic products in this discussion.

Both naphthalene and anthracene occur in the creosote oil fraction of tar. Creosote oil finds a ready sale here, the United States consumption being about two and one-half times the production, and it is evident that naphthalene and anthracene separated from the oil must be valued at the selling price of the oil. Starting at this value, it can be shown that, considering manufacturing costs and investment, the production of these materials in such state as is required by the manufacturer of dyestuff intermediates, does not give an adequate return when the products are sold at the prices which have prevailed on them when imported. This statement is not based on generalities or theory, but on experience, for we do produce certain amounts of refined naphthalene here, and know this condition accurately. Hence, under conditions prevailing up to the present, it has been evident to the tar distiller that he could not get a better return for the separated products than for the straight distillates.

It is but just to point out at this time the distinction between the coal-tar industry and the coal-tar chemical industry, which differentiates the production and use of tar, oils and pitch, etc., from that of the dyestuffs and drugs. While it is true that Germany has a highly developed coal-tar chemical industry, it is but little known or realized that the United States has developed the coal-tar industry to extents unthought of in Germany. Remember that an average tar yields 70 per cent of pitch and that in Europe, substantially the only use they make of this pitch is for fuel, while here over 90 per cent of the pitch is used in roofing, waterproofing and road making, and the development of the industry by the tar distiller is made evident.

So far there has been no real demand from dyestuff manufacturers for the separated tar products. The present dye manufacturers in this country have made only lines of dyes for special fields, starting with the so-called intermediate products, and they apparently did not contemplate the manufacture of those intermediates, so that their inquiries of the American tar distiller were entirely for intermediates such as anilin oil, beta naphthol, etc., which inquiries naturally would bring before the distiller the consideration of the other side of this subject, Why does not he work up these products himself?

But here the first consideration is providing outlets for excess materials. Up to the present there has not yet been an excess of the basic materials so that this inducement did not exist for the tar distiller. It must also be remembered that the products of tar which can be used in the manufacture of dyestuffs form but a small percentage of the tar and even if all of such products were separated for the manufacture of dyestuffs, there would still be over 90 per cent of the original tar to be disposed of by the distiller in his regular channels. And it must not be forgotten that the use of heavy chemicals, such as acids and alkalis, enters into the manufacture of dyestuffs in volumes largely exceeding the coal tar products involved, so that any inducement to the tar distiller to enter this field is secondary to the inducements offered the manufacturer of heavy chemicals.

The last consideration is that of the ultimate success of a large industry covering the entire field of dyestuffs. The magnitude of the project is sufficient reason why the tar distiller has not acted upon it, for to those who have given the question serious thought, it has become evident that only by duplicating the scale on which the foreign manufacture is carried on can we hope to finally compete with the established factories of Germany, and what prospect of growing to this magnitude would we have without protection during the years of growth? I mean by protection, not only adequate tariff protection, but also adequate protection against competitive methods aimed to crush the infant industry. Without such protection no man or group of men, however strong commercially, has yet had the temerity to plan for the investment of the millions of dollars required

to carry it through. And further, to make such a project successful, the coöperation of the textile trade, in fact, of all users of dyes, must be given. Not even a feeble indication of such coöperation was displayed before the conditions arose which showed this country's dependence on German dyestuffs.

Whether our industries shall have American-made dyestuffs from American coal-tar products depends largely on the consumers of dyestuffs. Their action or inaction will probably determine the answer.

BARRETT MANUFACTURING COMPANY  
FRANKFORD, PHILADELPHIA

### RELIEVING THE DYESTUFF CRISIS<sup>1</sup>

By BERNHARD C. HESSE

In the two and a half months that have elapsed since the outbreak of the European war there has been much agitation in the press, both lay and technical, for an increased production of coal-tar dyes in the United States. All users of coal-tar dyestuffs have known for as long as 40 years that the principal source of supply is Germany and they have also known of the various attempts made in this country to produce dyes in the United States. Just as the users of dyestuffs will invariably buy in the cheapest market and will not be swayed by motives of patriotism into paying a higher price for a domestic article than they would have to pay for an imported article so do American manufacturers and capitalists invest their money in American ventures which will pay them a profit, and they do not take hold of such enterprises through motives of patriotism only or of philanthropic benevolence toward their fellow man. Business is conducted for financial profit.

It required no imagination whatever to foresee that if for any reason our coal-tar dyestuff supply was shut off from Germany that coal-tar dyes in the United States would become scarce. Nevertheless, American users of dyestuffs have continued to use the imported article. The result is that even a few weeks after the outbreak of European hostilities the users in the United States became clamorous and hysterical and called out loudly for the American chemists to go in and make dyestuffs regardless of whether the American chemists were going to make money or not. The user has suggested to the maker that he increase his facilities, that he go to Congress and get a higher tariff and that he go to Congress for a change in the patent laws; however, the user has, on his part, not made any substantial offer of any effective help throughout these last two months. The chances are that, as in the past, the greatest opponents of increased tariff on dyes would be these self-same users. The users have confined themselves largely to fault-finding with American chemical manufacturers. The users say that their position is acutely distressing and they are facing serious hardships for want of dyestuffs and they want steps taken by others to see that they are never again placed in such position of hardship—no matter what the others may stand to lose.

To date, the suggestions from the users have been merely words and so far as the public is concerned there has been no effective action.

The users themselves decline to participate actively and financially in any dyestuff venture and they further decline to contract with prospective dyestuff manufacturers for even a portion of their requirements. In other words, their position is one of passive criticism—dead weight.

The domestic dyestuff makers are increasing their production as rapidly as circumstances will permit. At or about the end of 1912, 76 different chemical dyes were made in this country; today 100 such are made—in two years a 33 per cent increase; the United States market probably has no fewer than 900 different chemical dyes, each of them in active use, some of them to a very small extent, others to a very large extent and, no doubt, many of each of these could be eliminated and their places taken by others now on the market.

If the dyestuff users wish to encourage the domestic dyestuff makers they can at least disclose to the makers the extent of the market in the United States. The exact chemical dyes on the United States market and their individual consumption and prices paid are known collectively to two different classes. The importers collectively know it and the users collectively know it. It can hardly be expected that the importers are going to hand that information over to prospective makers, that is, to competitors. If the users want increased competition among the makers or want a more assured source of supply, then the least they can do is to place before the dyestuff makers of this country a list of all such dyes as are used in this country and the amount of each that is used annually, together with the price paid therefor. With such information before them those who make dyestuffs in this country can make intelligent provision for expansion of their business. To be sure, the makers could go to each and every user and ask him for the above information, but it is quite sure that that information would be refused. The users would decline to disclose to anyone their consumption of dyestuffs and the amount of their dyestuff account. If the users are really sincere and honest in their statement that they are in a plight and that they really do want increased production of dyes in this country, then the very least that they can do is to make a full and frank disclosure of what the possibilities and probabilities in the United States market are. As said before, there are over 900 different finished dyes that have to be made and before these 900 dyes are made something like 300 substances, themselves not dyes, have to be made; to ask the domestic chemical manufacturers to go down into their pockets for the capital to make each of these 900 dyes and each of these 300 things, themselves not dyes, and then to await the pleasure of the domestic dyestuff user as to whether he will take the goods or not is asking altogether too much from the makers on the part of the users.

If the users are afraid to disclose each to the other how much dye they use and what they pay for it they are certainly in a position to select some bank or trust company as a central confidential depository for such statements and let the bank or trust company make up from these separate statements a combined statement of the market and place that before the manufacturing public. If the dyestuff users will coöperate to that extent it is morally certain that an increase in production of dyes will take place with considerable rapidity. If the users decline to coöperate to this extent it is quite likely that the number of dyes manufactured will increase even in spite of the users, but the rate will be much slower. If the users want the rate of increase speeded up they must contribute their share, and probably a plan like that outlined above is as good as can be devised.

90 WILLIAM ST., NEW YORK

## CURRENT INDUSTRIAL NEWS

By M. L. HAMLIN

### THE PRESIDENT'S ADDRESS BEFORE THE CHEMICAL SECTION OF THE BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE

The address made by Professor William J. Pope, President

<sup>1</sup> Also printed in the *Textile Colorist*, Vol. 36, No. 430 (Oct., 1914).

of the Chemical Section of the B. A. A. S., is reported in the *Jour. Gas Lighting and Water Sup.*, 127 (1914), 506. The speaker pointed out that the investigator, continually occupied with his own problems, and faced with an ever-increasing mass of technical literature, ordinarily finds little time for reflection

upon the real meaning of his work, and secures, in general, far too few opportunities of considering in a philosophical sort of way the past, present, and future of his own particular branch of scientific activity. He then proceeded:

"It is not difficult to form a fairly accurate survey of the position to which chemistry had attained a generation—perhaps even a few years—ago. Probably no intellect now existing could pronounce judgment upon the present position of our science in terms which would commend themselves to the historian of the Twenty-first Century. Doubtless even one equipped with a complete knowledge of all that has been achieved, standing on the very frontier of scientific advance and peering into the surrounding darkness, would be quite incompetent to make any adequate forecast of the conquests which will be made by chemical and physical science during the next fifty years. At the same time, chemical history tells us that progress is the result, in large measure, of imperfect attempts to appreciate the present and to forecast the future. I, therefore, propose to lay before you a sketch of the present position of certain branches of chemical knowledge, and to discuss the directions in which progress is to be sought. None of us dare cherish the conviction that his views on such matters are correct; but everyone desirous of contributing towards the development of his science must attempt an appreciation of this kind. The importance to the worker and to the subject of free ventilation and discussion of the point of view taken by the individual can scarcely be overestimated.

"The two sciences of chemistry and physics were at one time included as parts of the larger subject entitled 'Natural Philosophy,' but in the early part of the Nineteenth Century they drew apart. Under the stimulus of Dalton's atomic theory, chemistry developed into a study of the interior of the molecule, and, as a result of the complication of the observed phenomena, progressed from stage to stage as a closely reasoned mass of observed facts and logical conclusions. Physics, less entangled in its infancy with numbers of experimental data which apparently did not admit of quantitative correlation, was developed largely as a branch of applied mathematics. Such achievements of the formal physics of the last century as the mathematical theory of light and the kinetic theory of gases are monuments to the powers of the human intellect.

"The path of chemistry, as an application of pure logical argument to the interpretation of complex masses of observations, thus gradually diverged from that taken by physics as the mathematical treatment of less involved experimental data, though both subjects derived their impetus to development from the speculations of genius. It is interesting to note, however, that during recent years the two sciences which were so sharply distinguished twenty years ago as to lead to mutual misunderstandings, are now converging. Many purely chemical questions have received such full quantitative study that the results are susceptible to attack by the methods of the mathematical physicist, while, on the other hand, the intense complication perceived during the fuller examination of many physical problems has led to their interpretation by the logical argument of the chemist, because the traditional mathematical mode of attack of the physicist has proved powerless to deal with the intricacies exhibited by observed facts.

"The progress of chemistry during the last century has been mainly the result of the coordination of observed facts in accordance with a series of hypotheses each closely related in point of time to the one preceding it. The atomic theory, as enunciated by Dalton in 1803, was a great impetus to chemical investigation, but proved insufficient to embrace all the known facts. It was supplemented in 1813 by Avogadro's theorem—that equal volumes of gases contain the same numbers of molecules at the same temperature and pressure. These two important theoretical developments led to the association of a definite

physical meaning with the idea of molecular composition, but ultimately proved insufficient for the interpretation of the ever-increasing mass of chemical knowledge collected under their stimulus.

"A further impetus followed the introduction by Frankland and Kekulé, in 1852 onwards, of the idea of valency and the mode of building-up constitutional formulae. The conception of molecular constitution thus arose as a refinement on the Daltonian notion of molecular composition. In course of time the theoretical scheme once more proved insufficient to accommodate the accumulated facts, until, in 1874, van't Hoff and Le Bel demonstrated the all-important part which molecular configuration plays in the interpretation of certain classes of phenomena known to the organic chemist.

"During the early days of chemical science—those of Dalton's time, and perhaps also those of Frankland and Kekulé—we can believe that chemical theory may have lacked the physical reality which it now seems to us to present. The attitude of our predecessors towards the theoretical interpretation of their observations was rather that described by Plato: 'As when men in a dark cavern judge of external objects by the shadows which they cast into the cavern.' In the writings of the most clear-sighted of our forerunners we can detect an underlying suspicion of a possibility that, at some time or other, the theory by means of which chemical observations are held together may undergo an entire reconstruction. A few years ago Ostwald made a determined attempt to treat our science without the aid of the molecular hypothesis, and, indeed, suggested the desirability of giving the Daltonian atomic theory decent burial.

"The last ten years or so have seen a change in this attitude. The development of organic chemistry has revealed so complete a correspondence between the indications of the conception of molecular constitution and configuration and the observed facts, and recent work on the existence of the molecule, largely in connection with colloids, with radioactivity, and with crystal structure, is so free from ambiguity, that persistence of doubt seems unreasonable. Probably most chemists are prepared to regard the present doctrine of chemical constitution and configuration as proved. Though they may turn a dim vision towards the next great development, they have few misgivings as to the stability of the position which has already been attained."

#### PATENT MEDICINES IN GREAT BRITAIN

Largely through the efforts of the American Medical Association and through legislation by Congress some progress has been made in the United States in limiting the dangers from the sale and use of secret remedies. The conditions are now worse in Great Britain than in this country, and in 1912 the government appointed a select committee which has just issued an abstract report. It finds [*Science*, 40 (1914), 374] that there is a large and increasing sale of patent and proprietary medicines and appliances and of medicated wines; that this constitutes a grave and wide-spread public evil and that an "intolerable state of things" requires new legislation to deal with it rather than merely the amendment of existing laws. Legislation is recommended as follows:

1—That every medicated wine and every proprietary remedy containing more alcohol than that required for pharmacological purposes be required to state upon the label the proportion of alcohol contained in it.

2—That the advertisement and sale (except the sale by a doctor's order) of medicines purporting to cure the following diseases be prohibited: Cancer, consumption, lupus, deafness, diabetes, paralysis, fits, epilepsy, locomotor ataxia, Bright's disease, rupture (without operation or appliance).

3—That all advertisements of remedies for diseases arising



from sexual intercourse or referring to sexual weakness be prohibited.

4—That all advertisements likely to suggest that a medicine is an abortifacient be prohibited.

5—That it be a breach of the law to change the composition of a remedy without informing the Department of the proposed change.

6—That fancy names for recognized drugs be subject to regulation.

7—That the period of validity of a name used as a trademark be limited, as in the case of patents and copyrights.

8—That it be a breach of the law to give a false trade description of any remedy, and that the following be a definition of a false trade description: "A statement, design or device regarding any article or preparation, or the drugs or ingredients or substances contained therein, or the curative or therapeutic effect thereof, which is false or misleading in any particular." And that the onus of proof that he had reasonable ground for belief in the truth of any statement by him regarding a remedy, be placed upon the manufacturer or proprietor of such remedy.

9—That it be a breach of the law: (a) To enclose with one remedy printed matter recommending another remedy. (b) To invite sufferers from any ailment to correspond with the vendor of a remedy. (c) To make use of the name of a fictitious person in connection with a remedy. (But it shall be within the power of the Department to permit the exemption of an old established remedy from this provision.) (d) To make use of fictitious testimonials. (e) To publish a recommendation of a secret remedy by a medical practitioner unless his or her full name, qualifications and address be given. (f) To promise to return money paid if a cure is not effected.

#### BRITISH FOREIGN TRADE IN AUGUST

As would be expected, the trade returns of the United Kingdom for August show a great reduction in both imports and exports. With Germany and Austria-Hungary trade has, of course, been extremely small, and that with other countries has been seriously interfered with. This has arisen more from the effects of the war on the foreign exchanges than from the war itself. During the month the value of the goods imported into Great Britain was \$206,000,000, which is \$66,000,000 (24.3 per cent) less than was imported during August, 1913 [*Engineering* (London), 98 (1914), 326]. Exports have, however, decreased from \$214,000,000 in August, 1913, to \$118,000,000 in 1914, the difference amounting to 45.1 per cent. The percentage drop in the value of re-exported goods is almost exactly the same. British imports from Germany have fallen from \$9,100,000 in August, 1913, to \$950,000 last month. More than half of this reduction—\$4,140,000—is accounted for by the diminution in imports of sugar; the figures for this commodity alone were \$4,350,000 in August, 1913, as against \$210,000 last month. Steel blooms, bars, girders, etc., account for another \$7,500,000 reduction, the imports being only \$245,000 last month. The total British exports to Germany have diminished from \$19,500,000 in August, 1913, to \$3,880,000 during August, 1914. The principal item is coal, the amount exported last August having been worth only \$368,000, whereas for August, 1913, the figure was \$2,320,000. Wool and woolen goods come next, these having fallen off from \$3,140,000 to \$1,380,000. Cotton yarn accounts for a further reduction of \$1,000,000. For iron and steel, the exports last August were \$224,000 as compared with \$480,000 for the same period last year. The only other item worth mentioning individually is textile machinery, which has fallen off from \$293,000 to \$195,000. Although these striking figures give a very good idea of the influence of the war on British trade with foreign countries, its full effects are somewhat masked by the fact that the returns include some goods imported and

exported before the declaration of war. The Royal Proclamation prohibiting the exportation of certain goods has also affected the figures.

#### SOME DATA OF GERMAN AND AUSTRIAN FOREIGN TRADE

The following data were published in London *Engineering* 98 (1914), 300, 331, 360. (1l = \$4.86.)

GERMANY'S EXPORTS OF SEWING AND KNITTING-MACHINES—A Board of Trade bulletin, recently issued, shows that Germany exports sewing and knitting-machines, and parts thereof, to a value of about 2,840,250l. per annum, while English exports are valued at 2,367,800l. The distribution is peculiar. England has the best of the Indian market, in which her sales amount to 128,550l., compared with Germany's 44,500l. To the Netherlands, German sales are valued at 78,300l., compared with England at 26,100l. In Sweden the respective sales are almost exactly reversed. In Belgium, Germany disposes of 117,200l. worth of these machines and parts; England sells there only 42,950l. worth. However, the tables are almost exactly turned in Spain, which buys from Great Britain to the value of 108,700l., and from Germany to the amount of 50,000l. Then, again, in Russia, England has a greater trade with sales amounting to 831,700l., compared with Germany's 399,300l.; but in Italy, Brazil and the Argentine, British business is much smaller than Germany's, as it is also in France, although in the latter country English sales amount to the considerable figure of 218,300l. Germany sends England machines and parts to the value of 136,200l. German machines find a ready sale in many countries, such as the United States, Mexico, Morocco, Bulgaria, Ecuador, etc., which markets seem to be scarcely touched by English manufacturers.

GERMANY'S EXPORTS OF PHOTOGRAPHIC MATERIALS—The value of the exports of photographic materials from Germany amounted in 1912 to 1,843,600l. The most important classes of goods dealt with were lenses, films, and chemicals. Sensitized paper and dry-plates were also exported in considerable, but lesser, quantities. Of photographic chemicals, Germany exported to the United States 72,900l. worth; to Russia, 79,950l.; and to England, 45,650l. Her largest exports of films were to France, which bought to the value of 110,550l., England taking 40,350l. worth. Next to Russia, Great Britain is Germany's largest customer for sensitized papers, taking nearly 40,000l. worth. The most important market for German optical glasses and lenses has been England, which took goods of this class to the value of 104,900l. Altogether, Germany sends England about 232,000l. worth of photographic goods in the year.

GERMAN AND AUSTRIAN TRADE IN BRASS AND BRASSWARE—Another white paper has recently been issued by the Commercial Intelligence Branch of the Board of Trade relating to the exports of brass and brassware by Germany and Austria. Compared with English exports in these trades, those of her rivals are enormous, though the available figures seem slightly less favorable to the United Kingdom than they actually are, since their figures cover certain articles not included in the English. As far as they form a guide, however, in a recent year, while the United Kingdom exported goods of this class to the amount of 1.6 millions sterling, Austria's exports were 1 million and Germany's nearly 6.5 millions. The principal exports of Germany were: Brass, tombac, and similar alloys, 549,650l.; rods, sheets, etc., of same, 1,088,700l.; wire of copper alloys, 314,200l.; lacquered and other wares of sheet brass, etc., 2,368,200l.; wares of copper, tombac, brass, etc., "verniet," colored, coated with nickel, etc., 1,075,000l. In many of these articles France and Italy are the largest purchasers from Germany, but in others Great Britain ranks as the largest buyer. In one or two cases Russia is Germany's largest market. Like previous reports, this one gives interesting information on the markets,

extracted from consular reports, etc., and all interested in enlarging their business while the opportunity offers would find these well worth perusal.

**GERMAN AND AUSTRIAN TRADE IN ANCHORS, GRAPNELS, AND CHAINS**—Germany has a considerable foreign trade in anchors and various types of chain both for ship and general use. Her exports in 1913 had a value of 165,700*l*. Excluding bicycle chains, the corresponding trade of Austria-Hungary for 1913 had a value of 11,910*l*. These figures are considerably below that of the United Kingdom for the same class of material, which in 1913 was 687,200*l*. The trade is one, however, with which England is well equipped to deal, and any efforts made at the present time to obtain the German share should have considerable chance of success. The subject is dealt with in one of the memoranda which are being issued by the Commercial Intelligence Branch of the Board of Trade to assist British manufacturers to find new outlets for their material during the war. The tables which are published show that, as far as ships' anchors, grapnels, and cables are concerned, the trade is chiefly in the hands of the United Kingdom, but that there would appear to be small openings for the sale of British-made articles in Russia, Roumania, and Turkey. For chains, other than ships' chains and cables, the United Kingdom holds an exceedingly strong position in the Australian, Indian, South African, Canadian, Japanese, and South American markets, as well as holding a large share of the trade in the Norwegian, Spanish, and Portuguese markets. In the Netherlands, Sweden, France, Russia, Roumania, and the United States there would, however, appear to be a possibility of extending British trade in these goods.

#### GERMAN RAILROAD MANAGEMENT

In an article in the *New York Railway Age Gazette*, on "German Criticism of State Railway Management," it is said that Germany's State railway management is an oppressive monopoly and a political mistake. Recently this view was expressed at three different industrial congresses, and in one case the indictment was backed by a two-thirds majority. This revolt against railway nationalization comes just at the time when some Americans and Englishmen have begun to see in nationalization an easy, infallible way out of all railway troubles. What aggravates the indictment is that it is mainly directed against the Prussian State system, which of all railway systems in Germany is the most flourishing and efficient. Every charge that is customarily levelled against corporation railway ownership is now (July 19) levelled against the Prussian State system. The main charge is that the Prussian system makes for monopoly and restraint of trade. In committing all the offenses which private corporations commit, the State knows no fear, for against it the public is doubly helpless, and there are no competing roads which can be used to bring the extortionate State to reason. German experience shows that State ownership does not prevent monopoly. Monopoly remains monopoly, even though it is managed by officials, and the State is only the national organ of erring men.

COMPOSITION OF THE GAS DURING CARBONIZATION (Per cent by volume)

	2	3	4	5	6	7	8	9	10	11	12	13	15	17	19	21	23	25	27	Heating gas
Hrc. coal carbonized	3.30	3.0	2.8	2.5	2.2	2.00	1.40	1.90	2.30	1.30	1.50	2.00	1.90	1.80	1.10	1.05	0.80	0.7	1.0	2.1
CO <sub>2</sub> .....	1.80	1.8	1.1	1.1	1.0	0.80	0.60	0.50	0.35	0.35	0.35	0.30	0.25	0.10						
C <sub>2</sub> H <sub>4</sub> .....	4.00	3.5	3.1	3.2	2.8	2.50	2.50	2.00	1.75	2.05	1.85	1.80	1.80	1.90	1.20	1.00	0.60	0.3	0.3	1.8
O <sub>2</sub> .....	1.05	0.8	0.6	0.6	0.5	0.50	0.40	0.20	0.20	0.20	0.10	0.20	0.15	0.25	0.15	0.05	0.05	0.1	0.3	0.6
CO .....	0.90	0.9	0.9	0.8	0.8	0.95	0.30	3.10	2.80	2.80	4.15	4.10	3.90	4.15	4.70	4.00	3.80	3.0	5.8	4.2
CH <sub>4</sub> .....	36.65	36.1	34.5	34.5	33.6	32.40	33.65	33.45	31.20	32.40	33.40	32.45	33.20	30.60	26.10	21.15	18.95	12.2	4.7	26.2
H <sub>2</sub> .....	42.50	44.6	48.8	47.8	50.1	50.75	53.75	50.55	47.10	51.50	50.65	49.75	53.40	51.60	55.75	58.95	61.90	67.0	70.0	51.7
N <sub>2</sub> .....	10.00	8.6	6.7	7.5	6.8	7.10	3.90	8.30	14.30	9.50	7.90	9.40	5.40	8.60	11.00	13.80	13.90	14.8	17.9	15.4
Min. cal. power (°C mm., 760 mm.), calculated per cubic meter	5402	5271	5086	5071	4971	4802	4906	4797	4324	4583	4660	4530	4665	4369	3978	4487	3412	2960	2419	3964

#### GERMAN CHEMICAL INDUSTRIES IN RUSSIA

The many factories and subsidiary companies maintained

by German chemical firms in Russia will be seriously affected by the war. The *Chemiker Zeitung* [38 (1914, 1914)] publishes a list of the more important of these. The Aktien-Gesellschaft für Anilin-Fabrikation has factories in Moscow and Libau, a subsidiary of the Hochster Farbwerke has headquarters in Moscow, the Chemische Werke Albert maintain factories in Sartana and Taganrog, and the Badische Anilin- und Soda-Fabrik has a large plant in Butirki near which are the Russian works of the Elberfelder Farbenfabriken; in 1906 the Aktien-Gesellschaft Renner, on account of tariff conditions, acquired, together with French and Russian firms, an extract factory in the neighborhood of Moscow; the Chemische Werke Riedel own a large block of the shares of the St. Petersburg A.-G. Pharmakon, and the Berlin firm of Schering has also large Russian interests.

The German iron industry also, according to the *Frankfurter Zeitung*, has important interests in Russia. Among the companies mentioned in this connection are the Milowiter Eisenwerk, the Donnersmarkhütte, the Oberschlesische Eisenbahnbedarf, the Oberschlesische Eisen-Industrie A.-G., the Metallfabriken Hanke and the Laurahütte.

#### THE MATCH INDUSTRY IN RUSSIA

The match industry in Russia has undergone a striking evolution since the beginning of the twentieth century. The *Chemiker-Zeitung* [38 (1914), 1000] states that while in the year 1902 ten factories manufactured over fifteen million phosphorus matches, in 1907 eleven factories manufactured less than a million, and in 1908 the production stopped almost entirely. Of the so-called mixed factories, manufacturing both phosphorus and safety matches, there were thirty-three in 1902 and in 1911 only two. The number of safety match factories increased in proportion to this decline, growing from eighty-three in 1902 with an output of over two hundred million, to one hundred and thirteen in 1911 with an output of more than three hundred million. The matches exported in 1911 were valued at \$675,000.

Russia is rich in wood suitable for matches and the manufacture of match sticks is a peasant house industry in the Government of Wjatka. The exports of these sticks in 1904, 1909 and 1911 amounted in round numbers respectively to \$325,000, \$274,000 and \$179,000.

#### TEMPERATURE CONDITIONS IN COKE OVENS

An important contribution to the literature of carbonization in coke ovens has lately been made in *Stahl und Eisen* by Professor Oskar Simmersbach, of Breslau. The experiments were carried out in a Koppers regenerative oven, and the temperature conditions existing during the period of carbonization and the composition of the volatile products were carefully determined. The following abstract of the article, with the tables, has appeared in the *Engineering Review*.

The oven was charged with 8 $\frac{3}{4}$  tons of coal containing 22.7 per cent of volatile matter, 6.32 per cent of ash, and 12.1 per cent of water. This yielded 79.86 per cent of coke. The coal was

carbonized for a period of 29 hours. The temperature rose gradually during this period, the concluding readings being

1090° C. at one-fourth the distance from the charging side, 1120° C. in the center, and 920° C. at one-fourth the distance from the discharging side. These temperatures correspond to the center of the carbonized mass. In the gas space above the coal, the finishing temperatures were respectively 870°, 860°, and 810° C. The resulting coke contained 88.53 per cent of carbon, 2.56 per cent of volatile matter, and 8.91 per cent of ash.

#### THE DISPOSAL OF RESIDUALS IN GAS AND COKE PLANTS

Difficulties are being experienced in England, according to the *Jour. Gas Lighting and Water Sup.*, 127 (1914), 563, both in gas-works and coke-oven plants with regard to the disposal of residuals. Ammoniacal liquor is difficult to dispose of since the usual buyers have been compelled, through force of circumstances, to stop the manufacture of their various products. Consequently they have not had sufficient storage room to accommodate the bulk of liquor offered. Those who make sulfate at their own works are placed in a rather more favorable position. Even though sulfate is not selling well just now, it is not a difficult matter to store it in large quantities, the principal objection being, however, that a large amount of money soon becomes locked up in the form of stocks. The disposal of tar, too, has not been unattended with difficulty. Again, lack of storage accommodation has been an important factor, the large distillers having had to restrict their operations owing partly to the embargo placed upon the export of creosote, and partly to the fact that the demand for pitch has been below normal. As far as benzol is concerned, no difficulty is reported. The increasing use of this product as an automobile fuel has created a good market, and this is particularly noticeable as soon as there is any talk of a petrol famine, or even of a substantial rise in price.

#### UNITED STATES MINERAL OIL EXPORTS

The *Journal of the Society of Chemical Industry* extracts from the number for August 3, of the *Oil, Paint, and Drug Reporter* the following particulars of exports of mineral oils from the principal customs districts of the United States (representing about 98 per cent of the shipments from all parts) during the twelve months, July 1, 1913, to June 30, 1914:

	Gallons	Value
Crude oil.....	146,056,086	\$6,808,513
Illuminating oil.....	1,155,809,430	74,374,091
Lubricating and paraffin oils.....	195,472,181	27,366,378
Naphthas, gasoline, etc.....	185,578,776	26,568,682
Residuum, gas oil, fuel oil, etc.....	586,301,600	15,562,192
Total, 1913-14.....	2,269,218,073	\$150,879,856
Total, 1912-13.....	1,947,746,303	134,514,109

#### TESTING MOTOR-CARS WITH TOWN GAS

According to the *Scientific American*, in consequence of the comparatively high cost of gasoline, and by way of reducing factory outlay, a number of Detroit makers have taken to testing their motors with town gas instead of with gasoline. It is found that an economy of as much as \$80 a day can be effected by some makers. Town gas at 45 c. per 1000 cubic feet is said to be cheaper for the purpose than gasoline at 5 c. a gallon. A comparison of costs reveals that an engine developing 19.04 horsepower consumes 458 cubic feet of gas, which costs 20.61 c. an hour, while 2.24 gallons of gasoline would be required to develop the same power, and the cost would be 33.6 c. an hour with gasoline costing 15 c. a gallon. On one test, it was proved that the cost of town gas works out at 58 per cent of the cost of gasoline.

#### SPELTER

The United States Geological Survey has recently issued a report that stocks of spelter increased by 23,380 tons in the first half of the year, and reached on July 1st the total of 64,039 tons. In the calendar year 1913 the production on the Continent of

Europe was 655,454 net tons, about 150,000 tons being exported to England. The British spelter production was 65,197 tons. It is considered that to furnish 150,000 tons to Great Britain per year would not strain the resources of the United States. The price of spelter rose 1 cent per pound at East St. Louis between August 6th and August 20th.

#### MINING IN SOUTH AFRICA

The report recently issued by the Royal Commission on Mining in South Africa states, according to *Engineering* (London), 98 (1914), 300, that the coal deposits in South Africa are numerous, but comparatively undeveloped. In 1913 the total output only amounted to 8,800,000 tons, valued at about \$10,000,000. The value of the output in diamonds in the Union of South Africa was \$55,000,000 in 1913, and in the same year the gold output from the Transvaal was valued at \$172,000,000. In regard to cost of production in the gold mines of the Witwatersrand it is said that by calculating the working capacity of two Europeans as equal to that of three natives, it is estimated that if natives at their present cost per shift—*viz.*, \$0.76 per head—had to be replaced by Europeans at \$2.40—and this appeared to be the minimum wage at which Europeans could live in the Transvaal—out of the fifty-two producing mines for which figures were available, twenty-six would cease to make a profit. If the white laborers replacing natives were paid at the rate of \$3.00, about the current rate in Western Australia, where living is cheaper, out of the fifty-two mines, thirty-five would cease to make a profit. The average cost of native labor, \$0.76 per shift, includes the cost of food, recruiting and compound expenses, in addition to money-wages. In 1913 the value of gold recovered per ton of ore, reckoned at the rate of \$20.64 per fine ounce, was \$6.74, in which sum the working costs per ton of ore were \$4.35 and the average gross working profit per ton of ore \$2.39.

The total amount paid in salaries and wages by the Rand gold-mines was \$66,000,000 in 1912, and \$63,000,000 in 1913. The average wage of the white employee, excluding the technical and clerical staff, was \$1,540 per year. That of the native was \$145. If to this latter sum there be added \$50 for housing the native and for the rations he receives, the white man, who is employed almost wholly in supervision, will be seen to receive about eight times as much in wage as the native, who does the manual work. The Economic Commission has found that, when allowance is made for the cost of living, the Witwatersrand workman is better off, in a monetary sense, than the workman in Australia and America, and much better off than the workman in Europe.

#### PLATINUM ORE IN SOUTHERN NEVADA

A deposit of ore, containing the platinum metals in greater quantity, and entirely dissimilar in occurrence to the earlier finds, has recently been discovered in the western portion of Clark County at the property of the Boss Gold Mining Co. This deposit, according to the *Engineering and Mining Journal* 98 (1914), 641, is 10 miles west of Goodsprings, in the Yellow Pine mining district, and only four miles from the California line. The ore varies in thickness from 2 to 10 ft., the average being about 6 ft., and in appearance is a brownish granular mass, showing occasional streaks of hard quartzose material. Both walls of the ore are shattered limestone, and along these walls occurs an encasement of malachite, varying in thickness from a few inches to several feet. The main body of the ore zone carries little copper. An average of the ore, sampled at 5-ft. intervals for 200 ft. along the upper tunnel, gave the following results: Gold, 1.13 oz. per ton; silver, 5.20 oz.; copper, 0.20 per cent. It has since been learned that this ore contains 0.5 to 1 oz. of platinum per ton.

In June, 1914, a winze was started from the upper tunnel following the ore on its dip, and high-grade ore was encountered



within a few feet. The appearance of the ore did not change materially except for the occurrence of small masses of greenish talc within the vein. Some of these masses were sufficiently large to be mined separately, and two small shipments, amounting to about one ton, were made, a settlement analysis of which was as follows, platinum not being determined or paid for: Gold, 124.79 oz. per ton; silver, 23.9 oz.; lead, 1.05 per cent; copper, 0.65 per cent; insoluble, 73.2 per cent; sulfur, 3.1 per cent; iron, 6.7 per cent.

On the same control sample of this shipment, the following was the result for metals of the platinum group: Platinum, 99.08 oz. per ton; palladium, 16 oz.; iridium, trace.

It has been fully determined that metals of the platinum group are present in all of the ore thus far developed, apparently as alloys of gold. It would also appear from numerous assays that the platinum metals bear a fixed ratio to the gold content, being in the proportion of about  $\frac{2}{3}$  oz. platinum to 1 oz. gold. The ore is thoroughly oxidized, no sulfides having as yet been recognized, and the gold alloys have a "rusty" appearance, showing no color after panning until they have been thoroughly scrubbed or treated with acid.

The occurrence of the ore is especially peculiar in that it occurs entirely in limestone, the nearest known porphyry contact being about 600 ft. distant.

From present development it would appear that the district bids fair to become an important producer of platinum, for numerous other claims have been located in the vicinity, and are now under development. The Azurite Mining Co., whose ground adjoins that of the Boss, has developed some ore, although of somewhat different character from that of the Boss mine.

#### SANITATION IN VERA CRUZ

The Vera Cruz correspondent of the *Journal of the American Medical Association* writes, according to *Science*, 40 (1914), 405, that the hot season, which is also the rainy season, begins in Vera Cruz in May or June and lasts till the end of September, and as the season advances the tendency is for the death and morbidity rates for all diseases to increase, owing to the heat itself and the rapid increase in the amount of malaria; yet thanks to the effective work of our sanatoriums, this year is an exception in that the civil death rate for July is practically no greater than for June, in which month it was lower than the average. The civil death rates per thousand of population per annum for the months of June and July for the past five years in the city of Vera Cruz are given below; the improvement for July of this year is too great to be accidental or due to anything but improved sanitation.

	June	July
1910.....	38.86	46.86
1911.....	38.29	46.86
1912.....	44.86	49.72
1913.....	36.86	41.15
1914.....	32.00	32.58

A comparative statement of the civil deaths from communicable diseases for June and July of this year is as follows:

	June	July
Typhoid fever.....	0	0
Malaria.....	8	2
Smallpox.....	4	1
Dysentery.....	12	4
Tuberculosis.....	19	26
Diarrhea and enteritis, under 2 years.....	19	14
Diarrhea and enteritis, 2 years and over.....	28	23

The increase of deaths from tuberculosis is not unusual during the hot weather; the smallpox epidemic is over and there are now no cases in the city; between May 18 and July 31, 66,432 persons were vaccinated; revaccinations are now being made when indicated but general vaccination ceased with the end of July. The principal gain is due to the fall in the death rates for malaria and intestinal diseases, and this improvement is directly due to our preventive measures.

The antimalarial measures which affect the civil population are three: the suppression of mosquito breeding, the use of the army laboratory in establishing the correct diagnosis, and the following up and treatment of all proved carriers of gametes in the blood. Mosquito breeding has been largely suppressed by the extensive and intricate system of ditches in the environs of the city, totaling about twenty-five miles in length; miles of vacant lots and hundreds of acres of swamp at the bases of the gigantic sand-dunes behind the city have been drained by the Health Department, and it is now possible to sleep comfortably in almost all parts of the city without the use of mosquito bars, something hitherto unknown in the height of the rainy season.

Malaria has been made a reportable disease by the Health Department and demonstration of the parasite in the blood is insisted on as far as possible. All houses where proven cases of malaria have occurred have been visited by inspectors trained in mosquito extermination, and secondary cases have been so far practically unknown. As a result of a partial malarial survey of the city, it has been found that the disease is principally localized along the railroad and railroad yards. Further investigations along this line are now under way. The work has advanced far enough to demonstrate that there is very much less malaria now than is usual at this time of the year; the Mexican physicians are unanimous in saying that the amount of *paludismo* is now very small.

The other group of diseases which have been brought under control are the dysenteries and diarrheas, and the preventive measures which seem to be directly responsible for the improvement are the following: the suppression of flies and the protection of food-stuffs in the market by screening, the improvement in the milk supply, and the disinfection and isolation of dysenteric cases. The number of milk venders in the city is approximately 150, and 200 samples of milk have been examined for dirt, adulteration and the percentage of fat. The milk examinations are made at irregular intervals on unannounced dates, each vender's milk being examined at least once quarterly. The measure, however, which seems most directly responsible for the diminution in the number of cases and deaths from intestinal diseases is the antify campaign. The city water has been frequently examined in the laboratory and found uniformly good. No cases of yellow fever have originated in Vera Cruz or been brought to that port.

#### NOTE

The description of the Fullagar internal combustion engine published in the last issue of *THIS JOURNAL*, 6 (1914), 862, was largely quoted from an article in the *Journal of Gas Lighting and Water Supply*, 127 (1914), 160. A full discussion of the theoretical principles involved can be found in *Engineering* (London), 98 (1914), 103.

## NOTES AND CORRESPONDENCE

#### NOTE ON ANTISEPTICS

Editor of the *Journal of Industrial and Engineering Chemistry*:

The recent discussion in these columns as to what ozone will or will not do to bacteria under different conditions suggests that many of the commonly accepted notions as to chemical

sterilization might be revised somewhat. In this connection, a few years ago, Owen,<sup>1</sup> of the Louisiana Experiment Station, showed that several of the well-known bacteria of the potato bacilli group—i. e., *Bacillus vulgatus*, *Bacillus mesentericus fuscus*, *Bacillus mesentericus niger* and *Bacillus mesentericus*

<sup>1</sup> *THIS JOURNAL*, 3, 481.

*granulatus*—were capable of growing in raw sugars and that the spores of two of the above species could withstand a temperature of 100° C. for two hours. Russel<sup>1</sup> recently recorded the fact that certain bacterial species tolerate phenol, cresol and hydroquinone, in fact appear to feed upon these substances. The author well remembers having seen well-developed mosquito larvae swimming about in a jar of bichloride of mercury solution, which had been made up in the usual manner for disinfecting utensils in a laboratory where investigations on cholera and other infectious diseases were being carried on. The director of the laboratory was so impressed that he had the solution analyzed in order to satisfy himself that there had been no mistake made in its preparation. What seems like a more remarkable case was noticed recently in this laboratory; *i. e.*, a mold growing on a solution containing 11.8 per cent of copper sulfate,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . Fragments of the mold growth first discovered grew on other samples of copper solution, showing that the first fully developed mold film had not accidentally dropped into the solution. Dr. Raymond F. Bacon, of this laboratory, states that he has observed molds derived originally from spoiled tomatoes, growing in a 10 per cent solution of sodium benzoate and also in a 10 per cent sulfuric acid solution. Perhaps these facts are not more remarkable than the oxidation of free sulfur to sulfate or the assimilation of atmospheric nitrogen and, doubtless, others could contribute equally noteworthy instances where certain bacteria, molds or low forms of life have appeared not to mind the presence of some of our commonly accepted antiseptics.

BENJAMIN T. BROOKS

MELLON INSTITUTE OF INDUSTRIAL RESEARCH  
UNIVERSITY OF PITTSBURGH  
October 8, 1914

#### NOTE ON WATER PURIFICATION BY OZONE

*Editor of the Journal of Industrial and Engineering Chemistry:*

The writer was much interested in the article on "Water Purification—With Report of the Ann Arbor Plant," by R. W. Pryer, that appeared in the October issue of *THIS JOURNAL*.

In reference to this report I would like to say that in April, 1910, I made a test of the Ann Arbor Plant for The Baltimore County Water and Electric Company, which was at that time installing an ozone plant somewhat similar in design to the one in question. The result of that test showed that the system, as it was then installed, was a failure as far as bacterial efficiency was concerned, although this inefficiency was ascribed to other causes than explained in Mr. Pryer's report. I do not know what changes have been made in the design or method of operation in the Ann Arbor plant since 1910, but the failure to produce efficient results (at that time) was due mainly to the intermittent action of the aspirators which caused a poor mixture of the ozone and water. No tests were made at that time as to the concentration of ozone produced at the plant, but from the odor it was not greater than 0.5 g. per cubic meter. The bacterial efficiency was practically nil and in some instances the number of bacteria was even greater than in the untreated water. This, as was explained by Mr. Pryer, was due to the breaking up of the suspended matter contained in the raw water, due to violent agitation in passing through the sterilizer.

The Ozone Plant of the Baltimore County Water and Electric Company, constructed under the supervision of Mr. A. E. Walden, although when first installed somewhat similar in design to the Ann Arbor Plant and built originally under the same patent right, has been greatly remodeled to overcome the faults encountered in the original design. The efficiency of the system has been greatly increased so that it is possible to obtain 99.0 to 100.0 per cent removal of bacteria, with a material reduction in color and organic matter. The concentration of the

ozone can be regulated from 0.3 g. to 5.0 g. per cubic meter. It has not been found economical, however, to use a concentration higher than 1.0 g., for with proper filtration prior to ozonization and thorough mixing of the gas with the water, efficient results can be obtained.

I regret that at the present time I am not at liberty to state just what the cost of sterilization will be, but it is far below any figures quoted by Mr. Pryer.

In my opinion the failure of ozone as a sterilizing agent for the purification of water has been mainly because of (1) the failure of the systems to give a thorough mixture of ozone and water; (2) the improper preparation of the supplies (where necessary) by efficient filtration previous to ozonizing; (3) the attempt to produce high ozone concentrations, with a greatly increased cost of operation, when by thorough mixing with proper devices a much lower concentration would serve the purpose.

S. T. POWELL

BALTIMORE COUNTY WATER AND ELECTRIC COMPANY  
BALTIMORE, MARYLAND  
October 8, 1914

#### WATER PURIFICATION BY OZONE—WITH REPORT OF ANN ARBOR PLANT—NOTE

*Editor of the Journal of Industrial and Engineering Chemistry:*

In *THIS JOURNAL*, 6, 797, the article on the purification of water by ozone with report of the Ann Arbor Plant is an interesting and painstaking description of the plant, which permits one to see clearly why it has never been a success. It is probable that the plant was built at a time when precise knowledge of the actual working of such plants was not extant or, at least, not generally available, and for this reason several errors, which at present appear obvious, were introduced into its design and construction.

The wells for ozonizing are seen to be about 3 ft. 3 in.  $\times$  3 ft.  $\times$  15 ft. deep and are 3 in number in each battery. It will, therefore, be seen that the period of contact between water and ozone is about 12 minutes and 45 seconds, which is far in excess of what is necessary to produce good ozonation, but on the other hand, the quantity of ozone used, namely, 0.227 g. per cm. of water, is perhaps  $\frac{1}{3}$  of what would be required in a system of the character of that in question. Also, it will be noted that the ratio of water to ozone is 1 to 2.2 and it is now known that the air should be in much larger quantity, both for the reason that the air itself is a value in the oxidation of organic matter and because the generation of ozone at high concentrations is decidedly uneconomical.

There are two types of ozone water purifiers used abroad to a considerable extent. I refer to the Otto and Siemens-de Frise methods. In the former, the ozonized air is introduced under the water by means of aspirating action of the latter in passing through a suitable suction pump, and as the amount of air that can be moved with a given flow of water is limited, we find that high ozone concentrations are made use of in this method of operating. In the de Frise method, as the ozonized air is introduced independently of the water by means of a separate compression pump, the amount of air that can be used is independent of the quantity of water that is used and we find, therefore, that large quantities of air are made use of and with benefit.

It will be noted that in the Ann Arbor Plant mica tubes are used in the ozone generators instead of glass, and we have found in our own experience that this is a very uneconomical form of ozone generator dielectric, the losses in mica being many times greater than the corresponding losses in glass. Furthermore, it will be noted that little or no effort has been made for cooling the generators, Mr. Pryer specifically mentioning

<sup>1</sup> *J. Soc. Chem. Ind.*, 1913, p. 1136.

that there is no water jacket provided for this purpose. This would have a decided adverse influence upon the economy of the ozone generators. The concentration of ozone generation, namely, 0.5 g. per cm. average, is not too high but on the contrary it is not as high as it should be to insure economical use of air.

While the plant as it stands is a failure, I should not hesitate to state that with the substitution of a new ozone generating plant of 10 kw. capacity, designed according to present knowledge along these lines, it could be made a complete success, using all of the structural work such as filter, fore bay, rear bays and ozone wells. In fact, one bank of wells, and perhaps two could be eliminated entirely and all of the ozone introduced efficiently into the water in one, or at most two, of the units now used.

M. W. FRANKLIN

SPRAGUE ELECTRIC WORKS, GENERAL ELECTRIC CO.  
BLOOMFIELD, N. J., October 20, 1914

### PRELIMINARY NOTE ON IRON IN FLORIDA SOILS

The total iron in seventy-three samples of Florida soils and other formations ranged from 0.23 to 11.53 per cent calculated as ferric oxide ( $\text{Fe}_2\text{O}_3$ ), the lowest figures representing material from the overburden of a phosphate mine and the latter a garden soil. The second largest amount was 7.44 per cent and only slightly greater than some succeeding ones. This indicates that the highest amount was probably due to added iron. The average iron content from all sources was 2.92 per cent.

Humus and iron, in general, were found to be present in direct proportion. Soils having much humus contained about 5.72 per cent iron oxide; those containing little humus contained about 3.72 per cent; those containing a trace of humus had 2.57 per cent; and those containing no humus contained about 1.57 per cent of iron oxide.

Untilled soils at depths of 3 and 9 inches contained comparatively more or less iron depending apparently upon the kind of plant life.

Roughly the amount of vegetation upon untilled soils was proportional to the iron content. Live oaks and hard woods were found to grow on soils containing 4.29 to 5.72 per cent iron oxide; cypress on soils containing about 5.7 per cent of iron oxide; long and short leaf pines and scrub oaks on soils containing 1.43 to 4.29 per cent iron oxide.

This work is being continued and the quantities of other elements are to be considered in relation to the iron.

We express our thanks to Dr. E. H. Sellards, State Geologist of Florida, and to Dr. J. McNeill of this Institution for samples of soil.

STATE COLLEGE FOR WOMEN  
TALLAHASSEE, FLORIDA  
August 18, 1914

C. A. BRAUTLECHT  
A. B. PARLIN

### NOTE ON COLORIMETRIC METHOD FOR VANADIUM

The writer has learned that some parties have not been successful in the use of the colorimetric method for vanadium in steel, described in *THIS JOURNAL*, 5, 736. It is stated that the colors as developed are dissimilar and therefore not comparable.

This difficulty is due to failure to thoroughly oxidize carbonaceous matter and to completely expel sulfur dioxide after reduction of the permanganate. In carrying out the determination, heat the solution strongly for 4 minutes after addition of permanganate; add sufficient dilute ammonium bisulfite to clarify the solution and continue heating 3 minutes, or until sulfur dioxide is entirely expelled. Upon cooling and finishing as directed, the colors are found to be very satisfactory for comparison.

LIMA, OHIO  
October 13, 1914

C. R. McCABE

### LUBRICANT FOR STOPCOCKS, ETC.

*Editor of the Journal of Industrial and Engineering Chemistry:*

An excellent lubricant for use with burette stopcocks, desiccators, etc., can be made by melting together equal parts of paraffin and vaseline. The paraffin gives body to the mixture which is therefore superior to vaseline alone, especially in places where high temperatures prevail.

632 DALE AVE., CLARKSBURG, W. VA.  
August 20, 1914

E. W. OSGERBY

### THE AMERICAN INSTITUTE OF MINING ENGINEERS

The annual meeting of the American Institute of Mining Engineers was held in Pittsburgh, Pa., on October 8th-10th, 1914.

After registration at the Hotel Schenley, the members in attendance were welcomed to the lecture hall of the Carnegie Institute by Dr. W. J. Holland, director of the Carnegie Museum; a technical session followed. The afternoon session of October 8th was devoted almost entirely to the presentation and discussion of papers. L. C. Morganroth discussed "The Occurrence, Preparation and Use of Magnesite," and then a paper on "The Iron Industry in Brazil," prepared by E. C. Harder, was read by Bradley Stoughton. During the course of Mr. Harder's paper, it was pointed out that few mineral deposits have in recent years attracted such wide-spread attention as the Brazilian iron ore deposits, owing mainly to the quantities of rich ore occurring there, in contrast to the ever-decreasing grade of ores shipped from many large producing iron ore districts. The Brazilian ore is of good grade, yielding 67 to 68 per cent of iron, and several hundred million tons are in sight. Up to the present, however, no iron ore has been exported from Brazil and only a very insignificant quantity has been used to supply the small domestic demand. G. S. Rice spoke on "Investigations of Coal-Dust Explosions," in the course of which he told of the history of investigations into various mine explosions from 1884 to the present time. In the evening of October 8th a formal reception was held in the lecture hall of the Carnegie Institute, after which T. T. Read exhibited a series of pictures illustrating "Ancient Methods of Manufacture of Iron in China," this was followed by a lecture on safety methods in coal mining by J. W. Paul, and then Edward Higgins explained two reels of pictures showing the mining of iron ore at Mineville, in the Adirondack region of New York.

The second day of the meeting opened with sectional sessions and closed with an informal dinner at the Hotel Schenley. In the interval between these assemblages, the 300 engineers in attendance were taken on inspection trips to various industrial plants and to the Government experimental mine at Bruceston. Albert Sauveur presided at the meeting of the iron and steel section. John Birkinbine read a paper on "Reserves of Iron Ore for the United States," in the course of which he stated that as far as the supply of ore is concerned there need be no fear for the future of the steel industry in this country. A report on "Finishing Temperatures and Properties of Rails," by George K. Burgess and others, and papers by J. K. Furst on the duplex process for making steel and by A. Sauveur on manganese steel, were next presented. At the meeting of the coal and coke section, R. V. Norris presided; papers were read by H. N. Eavenson, on coal mine explosions caused by gas and dust and by T. T. Read on the manufacture of coke. Heinrich Ries presided at the meeting of the section on non-metallic minerals, at which D. T. Day read a paper by W. C. Phalen on "Salt Making by Solar Evaporation." J. A. Dresser and O. B. Hopkins presented papers dealing with asbestos deposits. D. T. Farnham spoke on "Quarrying Shale by the Tunnel System," and H. A. Gardner and G. B. Heckel discussed paint pigments.



The meeting closed on October 10th after three sectional meetings and a visit to the oil and gas district about Oakdale and to the Pittsburgh Station of the Bureau of Mines. Edward Higgins read an interesting paper on the safety movement in the Lake Superior iron region; he said in part: "There are five organizations engaged in this work, namely, the mining companies, the county mine inspectors, the co-operative range committees, the Lake Superior Mining Institute, and the Federal Bureau of Mines. The unity of purpose and the strong co-operation that has characterized the work of the five bodies has been a factor in the development of the work. The bulk of the cost has been and still is borne by the mining companies. Mainly their work has been to provide protective devices in and about the mines and to educate the miners to protect themselves from injury." G. S. Rice read a paper prepared in conjunction with H. H. Clark, dealing with the dangers attending shot firing in coal mines when it is done without undercutting; he referred to the measures taken against this danger. J. C. H. Ferguson spoke of the evolution of grinding devices from the time of their preparation from cast iron to the present day of rolled steel shells. S. S. Rumsey spoke on centrifugal motor-driven mine pumps, and O. P. Hood discussed the use of gasoline locomotives and their effect upon the health of miners; Harrison Souder explained a new detonating fuse; J. V. Emmons read a paper on the surface decarbonization of tool steel, and R. H. Rice reported on a system of blast-furnace blowing. At the meeting of the section on petroleum and gas, C. H. Washburne presented a paper on "The Capillary Concentration of Gas and Oil," and L. Edelineau described his method of refining petroleum. These papers were followed by a general discussion of gas and oil wells.

W. A. HAMOR

#### THE NATIONAL COUNCIL FOR INDUSTRIAL SAFETY

The third annual meeting and congress of the National Council for Industrial Safety was held in Chicago on October 13th-15th, 1914. Over 2,000 delegates, representing various industrial concerns that are now giving practical demonstration of the "safety first" movement in their plants, were in attendance.

In addition to the formal meetings, there were round table sessions and exhibits of safety devices. The Congress was presided over by R. W. Campbell, chairman of the Central Safety Committee of the Illinois Steel Company, while W. H. Cameron, formerly of the American Steel Foundries Company, acted as secretary.

L. B. Burnett, assistant to the president of the Carnegie Steel Company, discussed "Effective Co-operation between Employer and Employee;" H. M. Wilson, engineer-in-charge, Bureau of Mines, Pittsburgh, Pa., spoke on "How Government Agencies May Best Co-operate with Manufacturers, Transportation Companies, and Others;" "Efficiency in Safety Work" was discussed by D. R. Kennedy, special agent of the Youngstown Sheet and Tube Company; R. H. Newbern read a paper on "The Safety Problem of the Railroads." A round table conference on the methods of educating workmen in accident prevention was led by L. R. Palmer, of the Pennsylvania Department of Labor and Industry; the economics sessions were presided over by C. B. Connelly. Addresses were made by Ida

M. Tarbell on "Effects of Safety on the Community," and by J. P. Jackson on "Safety First in Europe."

More than 2,000,000 serious accidents occur in the industries of the United States every year, and safety engineers are inclined to the belief that at least half of these may be avoided; the National Council for Industrial Safety has pledged itself to employ every known agency to co-operate in reducing these to a minimum.

W. A. HAMOR

#### AMERICAN LEATHER CHEMISTS' ASSOCIATION

The eleventh Annual Meeting of the American Leather Chemists' Association, in conjunction with the Annual Meeting of The National Association of Tanners, was held at the Hotel Sherman, Chicago, on October 28-31, 1914.

##### PROGRAM

President's Address. W. K. ALSOP.

Report of the Secretary-Treasurer. H. C. REED.

Committee Reports.

Color Valuation of Tanning Materials. GEORGE A. KERR.

Laboratory Apparatus for Leaching Experiments. LLOYD BALDERSTON AND W. K. ALSOP.

The Relation between Green Salted Weight and White Weight of Various Portions of the Hide. F. A. LOVELAND.

Lime. E. H. BACHTENKIRCHER.

Dyes and Dyestuffs. ALLEN ROGERS.

Leach House Efficiency. JOHN H. YOCUM.

Sewage Disposal and Use of Tannery Wastes. C. C. SMOOT, III.

A Résumé of the Methods of Tannery Sewage Disposal. A. ROTH, ROGERS.

The Bating of Hides and Skins. ALLEN ROGERS.

The Availability of Tannins in Liquors of Various Strengths. THOMAS A. FAUST.

Determination of Insolubles in the Analysis of Tannin Extracts. W. K. ALSOP.

Spruce Extract. SIGMUND SAXE.

The Clarification of Leather Extracts for the Determination of Reducing Sugars. F. P. VEITCH AND J. S. ROGERS.

General Meeting National Association of Tanners.

Discussion—Tanning School, Etc.—Joint Meeting with National Association of Tanners.

#### THE CHEMICAL SOCIETIES IN NEW YORK CITY

##### 1914-1915 SEASON—RUMFORD HALL, THE CHEMISTS' CLUB

American Chemical Society—October 9.

Society of Chemical Industry—October 23.

American Chemical Society—November 6.

Society of Chemical Industry—November 6.

JOINT MEETING—American Chemical Society, Society of Chemical Industry and American Electrochemical Society—December 11.

Society of Chemical Industry: Perkin Medal Award—January 22.

JOINT MEETING—American Electrochemical Society, American Chemical Society and Society of Chemical Industry—February 5.

American Chemical Society: Nichols Medal Award—March 5.

Society of Chemical Industry—March 19.

Society of Chemical Industry—April 23.

JOINT MEETING—Society of Chemical Industry, American Chemical Society and American Electrochemical Society—May 21.

American Chemical Society—June 11

## PERSONAL NOTES

The New York Section of the A. C. S. has appointed a committee composed of B. C. Hesse (Chairman), H. A. Metz, I. F. Stone, J. B. F. Herreshoff, D. W. Jayne, J. M. Matthews and A. Rogers to examine into the feasibility of expanding the manufacture of chemicals and dyestuffs in the United States and to report to the Section on November 6th.

The first meeting of the Maryland Section of the A. C. S. was

held at Hopkins Hall, Druid Hall Avenue, Baltimore, on October 10th. Dr. C. Glaser read a paper on "The Catalytic Decomposition of Bornyl Chloride by Copper."

The Society for the Promotion of Engineering Education will hold its 1915 meeting at the Iowa State College, Ames, Iowa, June 22-25th. Dean Marston of the Iowa State College is President of the Society.

The Pittsburgh Section of the A. C. S. met on October 15th at the Central Turn Verein where the following program was given: "The Separation of Gases by Fractional Distillation at Low Temperatures" demonstrated by experiments with Special Apparatus—G. A. Burrell; "The Uses of Hydrofluoric Acid in the Arts"—Dr. K. F. Stahl.

The Pittsburgh Section has offered its services to the manufacturing interests of Pittsburgh which are hampered by the present shortage of imported chemicals and other materials.

An addition is being built to the chemistry building of the University of California, costing, with its equipment, \$40,000. It will provide laboratory accommodation for 250 students.

The Rochester Section of the A. C. S. heard a lecture by Mr. H. E. Howe on "The Manufacture of Optical Glass" at its October 5th meeting.

The Wisconsin Section of the A. C. S. met on October 14th, when Prof. S. T. Acree, of the Forest Products Laboratory, spoke on "The Reactions of Both the Ions and the Molecules of Acids, Bases and Salts."

The office of the Secretary of the Society for the Promotion of Engineering Education has been moved to Pittsburgh and is now located in Thaw Hall, School of Engineering of the University of Pittsburgh.

The 27th meeting of the Nashville Section of the A. C. S. on Oct. 16th was a Memorial Meeting to William Lofland Dudley, with a paper on his life and work by Prof. J. T. McGill of Vanderbilt University.

The University of Illinois Section of the A. C. S. was addressed at its September 29th meeting by Prof. Edward Bartow, Director of the State Water Survey on "Some European Practice in Water and Sewage Purification, and Some Experiences in Europe after the Outbreak of War."

The Southern California Section of the A. C. S. met on October 15th at the Hollenbeck Hotel, Los Angeles. Mr. Edgar S. Baruch presented a paper entitled "Ethics and the Chemical Profession." The Committee on Oil Tests rendered an interesting report of their work of the past summer.

W. F. Monford has resigned from the St. Louis Water Works Staff and has established a laboratory at 506 North Vandeventer Ave. Mr. Monford will limit his work to the supervision and control of water supplies.

The Chicago Chemical Bulletin issued monthly by the Chicago Section of the A. C. S. presents an 8-page pamphlet, containing editorials, personals, advertisements, an employment column, correspondence and other items of interest to the Section.

The next meeting of the Chicago Section of the A. C. S. will be held on November 13th at the Hotel Sherman.

The Lexington Section of the A. C. S. held its 18th regular meeting on October 14th. Drs. Jos. H. Kastle and G. D. Buchner gave an Experimental Illustration of the Chemical Changes Occurring in the Accumulator by the Electrolysis of Cuprous Chloride.

The University of Illinois reports that its enrollment in Chemical Engineering and Professional Chemistry courses is forty per cent larger than ever before. There is also a large increase in graduate students in chemistry, particularly in industrial lines.

The Rochester Section of the A. C. S. met on October 19th, the subject for the evening being "What Can This Society Do for You?"

The St. Louis Section of the A. C. S. considered "The Effect of the War on American Chemical Industries" at its October 12th meeting. The discussion was led by Dr. F. W. Frerichs of the Herf and Frerichs Chemical Co., Dr. F. W. Russe of the Mallinckrodt Chemical Works, Mr. Gaston Du Bois of the Monsanto Chemical Works and Dr. J. R. Macpherson Klotz of the Barrett Manufacturing Co.

Mr. Luciano Selmi, formerly with the Lake Superior Iron & Chemical Co. at Ashland, Wisc., has accepted the position of Chief Chemist and Metallurgist with the Otis Steel Co., Cleveland, Ohio.

The San Francisco and Southern California Sections of the A. C. S. are considering the formation, jointly, of a Bureau of California Chemists to act as an Advisory Committee to manufacturers who may wish to engage in chemical industries on the Pacific Coast.

The Connecticut Valley Section of the A. C. S. holds its meetings the first Saturday of every month, October to May, inclusive, at the City Club of Hartford, 7 Central Row, Hartford, Conn. at 8 P.M. At its 26th meeting on October 3rd, Mr. Edwin C. Scott of the Solvay Process Co., Syracuse, N. Y., talked on Electro Cleaners and the general topic of cleansing.

On October 9th the corner-stone to the addition to the Chemical Laboratory of the University of Illinois was laid. The Hon. W. L. Abbott, President of the Board of Trustees, presided. After addresses by Prof. W. A. Noyes of the University and Mr. William Hoskins of Chicago, the corner-stone was laid by President Edmund J. James. When completed, the entire laboratory will be 231 feet long and 202 feet wide and will contain 164,288 square feet of usable space.

At the October 9th meeting of the Indiana Section of the A. C. S. at the Indianapolis Chamber of Commerce, Dr. W. M. Blanchard, President of the Section, spoke on "Diacyetyl and Some of Its Derivatives," giving the account of his research work in the University of Berlin last year.

The University of Michigan Section of the A. C. S. met on October 20th. Prof. E. E. Ware read a paper on "The Relation between China Wood Oil and Modern Varnishes."

Prof. Harry N. Holmes has resigned from the chair of Chemistry at Earlham College, Earlham, Indiana, where he has been since taking his doctor's degree at Johns Hopkins in 1907. Prof. Holmes is now head of the Department of Chemistry at Oberlin College.

At a joint meeting of the Pittsburgh Sections of the American Electrochemical Society and American Institute of Electrical Engineers, Prof. A. F. Nesbit, formerly of the University of Pittsburgh, discussed the Electrical Precipitation of Smoke, Dust, etc., and Mr. A. F. Weston, of the Research Corporation of New York City, showed lantern slides illustrating practical applications of the precipitation apparatus.

At the October 15th meeting of the Philadelphia Section of the A. C. S. the following papers were presented: "Glass and the Glass Industry" (illustrated), George E. Barton of the Whittall Tatum Co., Millville, N. J.; "Cork: Its Origin and Uses" (illustrated), H. W. Prentiss, Jr., of the Armstrong Cork Co., Philadelphia.

The Kansas City Section of the A. C. S. will meet on November 14th at the University of Kansas, Lawrence, when Prof. C. F. Nelson will speak on "Osmosis" and Prof. G. W. Stratton on "Chlorophyll."

Dr. David T. Day has resigned his position with the U. S. Geological Survey in order to engage in private practice.

The Second Pennsylvania Industrial Welfare and Efficiency Conference will be held in the State Capital at Harrisburg on November 17 to 19, 1914, under the auspices of the Pennsylvania Department of Labor and Industry and the Engineers' Society of Pennsylvania. The first conference, last year, was attended by about 2000 persons, many of whom were leaders in the labor and industrial world. An unusually effective Safety, Welfare and Efficiency Exhibition will be open from November 16th to 18th.

Mr. John D. Northup has been placed in full charge of gathering the statistics on petroleum and compiling this Government Report for the U. S. Geological Survey. Mr. Northup succeeds Dr. David T. Day, recently resigned.

# GOVERNMENT PUBLICATIONS

By R. S. McBRIDE, Bureau of Standards, Washington

**NOTICE**—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate. Consular Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington. The regular subscription rate for these Consular Reports mailed daily is \$2.50 per year, payable in advance, to the Superintendent of Documents.

## DEPARTMENT OF AGRICULTURE

**Arsenical Cattle Dips: Methods of Preparation and Directions for Use.** ROBERT M. CHAPIN. Farmers' Bulletin 603, from the Bureau of Animal Industry. 16 pp. A popular write-up suitable only for the parts of this country infected with the Texas fever tick.

**The Application of Refrigeration to the Handling of Milk.** JOHN T. BOWEN. Department Bulletin 98, from the Bureau of Animal Industry. 88 pp and 37 figs. Paper, 10 cents. This paper "discusses the application of refrigeration in the operation of the modern milk plant and describes the various forms of mechanical and other systems of cooling." It is of interest to producers, shippers, dealers, and consumers of milk generally, and also to manufacturers of refrigeration machinery and appliances.

**Harmful Effects of Aldehydes in Soils.** OSWALD SCHREINER AND J. J. SKINNER. Department Bulletin 108, from the Bureau of Soils. 26 pp. Paper, 10 cents. "This bulletin deals with the discovery and properties of aldehydes in soils. These are shown to affect crops unfavorably and decrease the yield greatly. The results are of interest to agricultural experimenters and those practical farmers whose training interests them in the advance of scientific agriculture."

**The Inorganic Composition of Some Important American Soils.** W. O. ROBINSON. Department Bulletin 122, from the Bureau of Soils. 27 pp. Paper, 5 cents. "This bulletin gives the results of chemical and mineralogical investigations of certain important soils. The inorganic part alone is considered and special attention is given to the so-called rare elements. It is technical and intended for the use of research workers in agricultural chemistry and teachers in the same field. It will also be found of secondary interest to practical agriculturists."

**Absorption of Fertilizer Salts by Hawaiian Soils.** WM. McGEORGE. Bulletin 35, of the Hawaii Experiment Station. 32 pp. Paper, 5 cents.

**Oxidases in Healthy and in Curly-dwarf Potatoes.** H. H. BUNZEL. Separate from the Journal of Agricultural Research, 2, 373-404. A contribution from the Bureau of Plant Industry.

**Moisture Tester for Grain and Other Substances and How to Use It.** J. W. T. DUVEL. Circular 72, reissued with supplement. 16 pp. Paper, 5 cents.

**Composition of Roquefort-cheese Fat.** JAMES N. CURRIE. Separate from the Journal of Agricultural Research, 2, 429-34.

**The Effect of Strongly Calcareous Soils on the Growth and Ash Composition of Certain Plants.** P. L. GILE AND C. N. AGERTON. Bulletin 16 of the Porto Rico Agricultural Experiment Station. 45 pp. Paper, 10 cents.

**Density of Wood Substances and Porosity of Wood.** FREDERICK DUNLAP. Separate from the Journal of Agricultural Research, 2, 423-8.

**Effects of Certain Cooking Conditions in Producing Soda**

**Pulp from Aspen.** HENRY E. SURFACE. Department Bulletin 80, from the Forest Service. 63 pp. Paper, 15 cents. The detailed information presented is of interest in connection with laboratory experimental work as well as to those endeavoring to improve the efficiency of commercial paper-making plants using the soda process.

**Relative Resistance of Various Conifers to Injection with Creosote.** C. H. TEESDALE. Department Bulletin 101, from Forest Service. 43 pp. Paper, 15 cents. This bulletin is intended to show "how woods should be graded in order that they may give uniform results when subjected to treatment with preservatives; it is intended for those interested in wood preservation."

**Yields from Destructive Distillation of Certain Hardwoods.** L. F. HAWLEY AND R. C. PALMER. Department Bulletin 129, from the Forest Service. 16 pp. Paper, 5 cents. This bulletin gives the results of laboratory distillation tests; it is of interest to manufacturers of by-products.

## HYGIENIC LABORATORY

Bulletin 96, dated August 1914, contains the following articles of chemical interest. 124 pp. Paper, 15 cents.

(1) Report of Investigation of Coastal Waters in the Vicinity of Gulfport and Biloxi, Miss., with Special Reference to Pollution of Shellfish. R. H. CREEL.

(2) Comparison of Methods for Determination of Oxygen in Waters in Presence of Nitrite. ELIAS ELVOVE.

(3) Some New Compounds of the Choline Type, Including the Preparation of Monoacetate of  $\alpha,\beta$ -Dioxy- $\beta$ -methyl Butane. G. A. MENGE.

(4) Detection of White Phosphorus in Matches. EARLE B. PHELPS.

(5) Chemical Composition of Rubber Used in Nursing Nipples and in Some Rubber Toys. EARLE B. PHELPS AND ALBERT F. STEVENSON.

(6) Analysis of Thymol Capsules. ATHERTON SEIDELL.

(7) Seasonal Variation in Composition of Thyroid Gland. ATHERTON SEIDELL AND FREDERIC FENGER.

(8) Note on New Apparatus for Use with Winkler Method for Dissolved Oxygen in Water. HYMAN L. SHOUB.

(9) Pharmacological Action of Some Serum Preservatives. CARL VOEGTLIN.

## PUBLIC HEALTH SERVICE

**Studies on the Self-purification of Streams.** EARLE B. PHELPS. Reprint 214, from the Public Health Reports. 5 pp. Paper, 5 cents. This article describes the physico-chemical principles upon which are based the investigations of re-aeration of streams and the limits of permissible pollution without nuisance. It is a condensed form of the paper presented at the Cincinnati meeting of the American Chemical Society. (See THIS JOURNAL, 6, 682.)

**Biological Products Establishments, Licensed Propagation and Sale of Viruses, Serums, Toxins, and Analogous Products.** Reprint 206, from the Public Health Reports. 4 pp. Paper, 5 cents.

## SUPERINTENDENT OF DOCUMENTS

Lists have been issued recently by this office giving the government publications for sale by the Superintendent of Documents on various phases of Agricultural Chemistry (Price list 40, 6th edition) and Forestry in the United States (Price list 43, 6th edition). Either of these lists can be obtained on request.

## BUREAU OF FOREIGN AND DOMESTIC COMMERCE

**Cost of Production in Pottery Industry, Summary of Results** Miscellaneous Series 16. 43 pp. Paper, 10 cents.



**Cottonseed Products and Their Competitors in Northern Europe. Part 2, Edible Oils.** ERWIN W. THOMPSON. Special Agents Series 89. 31 pp. Paper, 5 cents.

Those interested in **South American and similar trade conditions** will find information of value in the following four publications:

(1) **Banking and Credit in Argentina, Brazil, Chili, and Peru.** EDWARD N. HURLEY. Special Agents Series 90. 72 pp. Paper, 10 cents.

(2) **Important Details in South American Trade.** Separate from Daily Consular and Trade Reports, August 28, 1914. 4 pp.

(3) **Publications on Latin America and West Indies.** Miscellaneous Series 17. 15 pp. Paper, 5 cents. This gives a brief review of the information available to manufacturers and exporters in the bulletins issued by the Bureau.

(4) **Commercial Relations of the United States with Foreign Countries, calendar year 1912.** (A special unnumbered publication). 272 pp. Cloth, 40 cents.

The Monthly Summary of Commerce and Finance of the United States has become the **Monthly Summary of Foreign Commerce of the United States**; the number for July, 1914, is the first of this new title; it is also No. 1 of the 1914-15 series.

#### BUREAU OF STANDARDS

**The Relation of the Horse-power to the Kilowatt.** Circular 34, 2nd edition. 16 pp. This circular includes a full discussion of the present practice in power ratings; the use of the kilowatt instead of the horse-power is urged.

**The Testing of Potentiometers.** FRANK WENNER and ERNEST WEIBEL. Scientific Paper 223. 40 pp. This paper includes a discussion of the theory of potentiometer measurements as well as the methods of testing which are described.

**The Emissivity of Metals and Oxides. I. Nickel Oxide (NiO) in the Range 600° to 1300° C.** G. K. BURGESS and P. D. FOOTE. Scientific Paper 224. 24 pp. Results for the monochromatic emissivity or absorptivity are given for the above range, and for the dispersion for 4 temperatures.

**Adjustments of the Thomson Bridge in the Measurement of Very Low Resistances.** F. WENNER and E. WEIBEL. Scientific Paper 225. 4 pp. A description of two methods of procedure for making this adjustment.

#### BUREAU OF MINES

**Experiments with Furnaces for a Hand-fired Return Tubular Boiler.** SAMUEL B. FLAGG, GEORGE C. COOK and FORREST E. WOODMAN. Technical Paper 34. 32 pp. The investigation reported was confined to the construction and operation of furnaces of this one type; the results are of greatest interest to the mechanical engineer.

**Waste of Oil and Gas in the Mid-continent Fields.** RAYMOND S. BLATCHLEY. Technical Paper 45. 57 pp. This report "describes the general amounts and kinds of wastes, and attempts to show the importance of conserving these natural resources. It does not present general rules and regulations for reducing the waste of gas and oil, except in two extreme cases, but suggestions are made that are intended to help the operator meet the situation. The right kind of cooperation should accomplish more than the enactment of drastic regulations."

**Report of the Committee on Resuscitation from Mine Gases.** W. B. CANNON, GEORGE W. CRILE, JOSEPH ERLANGER, YANDELL HENDERSON and S. T. MELTZER. Technical Paper 77. 36 pp. This report discusses the several manual and mechanical methods for artificial respiration, including recommendations.

**Prevention of Accidents from Explosives in Metal Mining.** EDWIN HIGGINS. Miners' Circular 19. 16 pp. A non-technical discussion of the subject.

**Supplementary List of Permissible Explosives.** (Unnumbered circular). 1 p. The additions to the list up to August 1, 1914, are given.

**Origin of Coal.** DAVID WHITE and REINHARDT THIESSEN. Bulletin 38. 390 pp. including 54 plates. Paper, 80 cents. The following articles on phases of the general subject make up this bulletin: **Geologic relations of the coals.** Analyses of the coal samples studied under the microscope. **Physiographic conditions attending the formation of coal.** **Rate of deposition of coal.** **Regional metamorphism of coal.** **Origin and formation of peat.** **Microscopic study of coal.**

#### GEOLOGICAL SURVEY

**Geology of the Phosphate Deposits Northeast of Georgetown, Idaho.** R. W. RICHARDS and G. R. MANSFIELD. Bulletin 577. 76 pp. Although largely of geological interest, this bulletin includes a brief statement of the chemical character, specific gravity, and possible sources of these phosphate deposits.

Advance chapters of "Contributions to Economic Geology" have recently been issued as follows, the first seven titles being from the second part of the issue for 1912, the remainder from the first part for 1913:

(1) **Geology and Coal Resources of the Sierra Blanca Coal Field, Lincoln and Otero Counties, New Mexico.** CARROLL H. WEGEMANN.

(2) **Coal near Thompson, Grand County, Utah.** FRANK R. CLARK.

(3) **Coal near Wales, Sanpete County, Utah.** FRANK R. CLARK.

(4) **Rhode Island Anthracite.** G. H. ASHLEY.

(5) **Coking Coal in Powell Mountain, Scott County, Va.** M. R. CAMPBELL.

(6) **The Coal Resources and General Geology of the Pound Quadrangle of Virginia and Kentucky.** CHARLES BUTTS.

(7) **The Coal Resources of a Part of Northeastern Missouri.** F. C. GREENE. Each of these articles includes analyses of the coals and data of economic interest.

(8) **Some Deposits of Mica in the United States.** DOUGLAS B. STARRETT. Bulletin 580F. 60 pp. This paper reports on the investigations made of a number of mica deposits studied during 1913; it does not give a general report on the whole country, but some information of a general nature as to the production, uses, value, and nature of mica is included.

(9) **Gold Placers on Wind and Bighorn Rivers, Wyoming.** FRANK C. SCHRADER. Bulletin 580G. 20 pp.

(10) **Carnotite near Mauch Chunk, Pennsylvania.** EDGAR T. WHERRY. Bulletin 580H. 5 pp.

**Colorado Ferberite and the Wolframite Series.** Bulletin 583. 75 pp. with 49 figures and plates. This bulletin is made up of two articles: "The mineral relations of ferberite" by F. L. Hess and "Crystallography of ferberite from Boulder County, Colorado" by W. T. Schaller.

**Bibliography of North American Geology for 1913.** J. M. NICKELS. Bulletin 584. 193 pp. The list is arranged alphabetically by authors' names, but a subject index is included. It contains a list of chemical analyses reported and of the minerals, rocks, and formations described.

**Our Mineral Reserves—How to Make America Industrially Independent.** G. O. SMITH. Bulletin 599. 48 pp. This bulletin is issued "for the purpose of furnishing to the public in convenient form a summary of the mineral resources available for utilization under the pressure of present conditions, in the hope of encouraging their development and discouraging the importation of raw material and products which can be supplied at home."

**Mineral Resources of Alaska, 1913.** Bulletin 592. The advance chapters of this annual publication are now being issued. The whole report is made up of 21 papers by 11 authors; one of the papers is an administrative report, two are general summaries, and the others deal more specifically with the economic geology of certain districts. Separates have been issued for the following parts of this report:

(A) **The Mineral Deposits of Alaska and the Alaskan Mining Industry in 1913.** ALFRED H. BROOKS. 57 pp. In the first part of this are described the geologic occurrence of the following: Gold, copper, silver, zinc, lead, tin, tungsten, iron, chromite, antimony, other metallic minerals, coal, petroleum, peat, structural materials, and miscellaneous nonmetallic minerals. In the second section the details are given of operations for 1913, which show some falling off of mineral production as measured by total value of the output. The following gives the more interesting data:

MINERAL PRODUCTION OF ALASKA IN 1913

	Quantity	Value
Gold (fine ounces).....	755,947	\$15,626,813
Silver (fine ounces).....	362,563	218,988
Copper (pounds).....	21,659,958	3,357,293
Coal (short tons).....	2,300	13,200
Marble, gypsum, tin, lead, petroleum, etc. ....	.....	200,000

Total.....\$19,416,294

(C) **Marble Resources of the Juneau, Skagway, and Sitka Districts.** ERNEST F. BURCHARD.

(D) **A Barite Deposit near Wrangell, Alaska.** ERNEST F. BURCHARD.

(E) **Mineral Deposits of the Yakutat District, Alaska.** A. G. MADDREN.

(K) **Mineral Resources of the Yukon-Koyukuk Region, Alaska.** HENRY M. EAKIN.

Most of the other separates are primarily of mining interest, having little of chemical interest.

**Quality of the Surface Waters of Washington.** WALTON VAN WINKLE. Water-Supply Paper 339. 105 pp. This is one of a series of papers frequently issued by the Geological Survey, treating of the water supplies of some part of the United States. This paper gives many analyses and includes "a brief discussion of the constituents, uses, and purification of natural waters and a detailed consideration, by drainage basins, of the quality of the streams of Washington, showing the nature and the amount of the material which they hold in solution."

**Surface Water Supply of the United States, 1912.** This series of papers for different parts of the country contain results of stream flow measurements and other data gathered at the numerous gaging stations. Little data of chemical interest is given; the papers of this series should not be confused with those of the series described just above.

CONSULAR REPORTS—SEPTEMBER, 1914

The production of **geranium oil** in Algeria and its chemical constants and adulterants are described. (P. 1195.)

**Perfume essence** from the Reunion Islands include geranium oil, cananga oil, and verti-vert. (P. 1197.)

A new **paper factory** is being constructed at Maracay, Venezuela. (P. 1223.)

**Portland cement** factories of Japan are exporting cement to Manchuria and China. (P. 1227.)

The annual production of **ammonium sulfate** in Japan is nearly 20,000 tons; the imports are about 120,000 tons. (P. 1228.)

It is reported that the embargo on exportation of **potash** from Germany via Holland has been removed. (P. 1261.)

Plans have been completed for the new **University of British Columbia** to be located near Vancouver. A contract has been let for a science building to cost \$600,000.

The Chilean government will introduce **oil-burning locomotives** on 125 miles of the government railway as an experiment. (P. 1295.)

Both **oil and electric safety lamps** are used in the Cardiff (Wales) coal mines, though the miners do not readily accept the electric lamps. (P. 1342.)

**Gas** is being made from low-grade coal mine refuse at Nanaimo, Canada, and is piped 60 miles to Victoria. (P. 1366.)

Exportation of **potash** from England has been forbidden. (P. 1457.)

The use of **high pressure gas** for street lighting is being considered for Bombay. (P. 1461.)

The methods of mining **graphite** in Ceylon are described and the trade conditions and uses of graphite are discussed. (P. 1462.)

Imports of **dyestuffs** into the United States have been practically constant in amount for the past five years, about \$10,000,000 annually. In 1909 there were manufactured in this country about \$16,500,000 worth of dyestuffs, making the total consumption over \$25,000,000 worth. (P. 1469.)

The frequency of **lead poisoning** in the British pottery industry has decreased from 66 per 1000 employees in 1898 to 14 per 1000 in 1912. (P. 1477.)

DEMANDS FOR AMERICAN GOODS OWING TO THE WAR (PP. 1)

HONDURAS—1224 and 1361	JAPAN 1881 and 1891	CHINA 1616, 1627, and 1661
Crockery	Aniline dyes	Dyestuffs
Enamel ware	Potassium chlorate	Chemicals
Essential oils	Phosphorus	Paper
Cornstarch	Rosin	Enameled ware
Baling	Aluminum	Glass
Candles	Copper, zinc, nickel and iron articles	Phosphorus
Medicines	Dynamite	Potassium chlorate
Vegetable oils	Grease	Fertilizers
BIRMINGHAM, ENG- LAND—1311, 1414, 1484 and 1629	GREECE—1590 and 1614	SUGAR
Wire rods	Sugar	PORETOCOAL 1626
Steel billets	Copperas	Drugs
Spelter	Coal	Chemicals
Copper and brass tubes	Coal	Coal
Brass wire and sheets	Iron manufactures	Glass
Bottles	Cotton-seed oil	Litholeum
Sulfur	Oleomargarine	Paints
Print paper	SPAIN 1590 and 1614	JAMAICA 1628
Gold leaf	Coal	China
Gas mantles	Iron and steel	Drugs
VENEZUELA—1443	Phosphate	Glass
Bottles	Glass	Gas mantles
Paper	Cement	Match-box
Leather	Starch	Iron, tin, copper, galvanized, and enameled ware
Drugs	Dyes	ARGENTINE 1633-42
Iron	Photographic supplies	Coal
Paint	Petroleum	Paper
Kerosene	Paper	Calvanized iron
Sterin	ARABIA—1590	Enameled iron
Copper plate	Dyestuffs	Glassware
Olive oil	Gasoline	Crockery
WEST INDIES—1550, 1591, and 1677	Kerosene	Photographic supplies
Electrical supplies	Soap	Drugs
Chemicals	Cement	Chemicals
Metal goods	Glass	Cement
Cement	Iron	Plate glass
Drugs	Coal	
Cotton seed oil	Pottery	BELGIAN CONGO 1591
Kerosene	Wine	1591
Gasoline	Petroleum	CHOSSEN, KOREA 1591
Coal	Coal	Kerosene
CANADA 1550, 1591, and 1613	Explosives	Paper
Drugs	Metals	Drugs
Chemicals	NEW ZEALAND—1591	Drugs
Metal ware	Drugs	Chemicals
Paint colors	Enameled ware	Glass
Plastic glass	Paper	SUGAR
Zinc	Aluminum	INDY 1615 and 1661
Lead	SWITZERLAND 1615	Glass
Tin	Cotton-seed oil	Chemicals
Dyes	Petroleum	Drugs
NORWAY—1551, 1590, and 1594	Gasoline	Metals
Sugar	Sugar	Lubricating oil
Tin plate	India 1615 and 1661	Cement
Materials for oleomargarine	Glass	Carbonates
Hardware	Chemicals	Sulfur
Rubber	Drugs	Chloride of lime
Zinc	Explosives	Sodium and potassium carbonates
Chemicals	Rubber goods	Gasoline
Dyes	NETHERLANDS—1626	Petroleum
Sulfur	Hides	Coal
Soda	Enameled ware	Copper
EGYPT 1551	Petroleum	Rosin
Beer	Paints	Oil cake
Mineral waters	Paper	Sodium hydrosulfide
Oleomargarine		SO. TH. AFRICA 1674 and 1677
Copper		Explosives
Brass		Asbestos
Iron and steel		Cement
Scientific instruments		Calcium carbide
Glass		Carbon dioxide
Petroleum		Potassium and sodium cyanides
Coal		Disinfectants
Chemicals		Sugar
Paints		Tartaric acid
Paper		Glass
		Glycerine
		Sulfat
		Fertilizers
		Nitrates
		Lubricating oil
		Paper
		Photographic supplies
		Silver plate
		Sheep dip
		Tea
		Tin ware
		Zinc
		NICARAGUA—1725
		Iron ware
		Chemicals
		Paper
		Drugs
		Soap

## STATISTICS, ETC., ON EXPORTS TO THE U. S. (PP.)

GHENT, BELGIUM  
1191  
Chicory  
Glue stock  
Machics  
Naphthalene  
Cocoa oil  
Copra oil  
Creosote oil  
Paper stock  
PEKU—1218  
Sugar  
Rubber  
Guano  
Hides  
Silver  
Copper  
Vanadium  
Gold  
SWRIA—1237  
Brandy  
Butter  
Olive oil  
Pistachio nuts  
Hides  
TUNGTAU, CHINA—  
1274  
Soya-bean oil  
Egg products  
Ground-nut oil  
Hides  
Silk  
Walnuts  
ASATIC TURKEY—  
1301-2  
Colocynth  
Pur  
Galls  
Skins  
Licorice  
HONDURAN—1313-27  
Hides  
Gold  
Silver  
Liquid amber  
Peppermint balsam  
Rubber  
Sarsaparilla  
HONGKONG—1304  
Aniseed oil  
Camphor  
Cassia  
Cassia oil  
Cement  
Earthen ware  
Glass ware  
Lard  
Matches  
Peanuts  
Peanut oil  
Silk  
Sugar  
Tin  
PANAMA—1328-38  
Balata  
Cocobolo  
Copper  
Hides  
Ipecac  
Ivory nuts  
Pearls  
Rubber  
VENICE—1431  
Beet pulp  
Garlic  
Glass  
Glycerine  
Hemp

AIN, LA CHAPELLE  
1452  
Bleaching powder  
Fire brick  
Chemicals  
Cocoa butter  
Marble  
Dyes  
Paint driers  
Fertilizers  
Ruses  
Paper  
Soap  
Steel  
Tin ware  
Mineral water  
Wine  
JAPAN—1489-1501  
Albalone  
Antimony ore  
Soya-bean oil  
Camphor  
Coal and coke  
Copper  
Graphite  
Hides  
Vegetable isinglass  
Drugs  
Paper  
Peanuts  
Peppermint oil  
Silk  
Sulfur  
Vegetable wax  
BARMEN, GERMANY—  
1456  
Chemicals  
Dyes  
Coke  
Hides  
Nickel  
MAGDEBURG, GER-  
MANY—1505-17  
Barium hydroxide  
Carbon tetrachloride  
Bone-black  
Copper products  
Fertilizers  
Kainite  
Kieserite  
Magnesium chloride  
Magnesium sulfate  
Peanut oil  
Potassium carbonate  
Potassium hydroxide  
Potassium cyanide  
Potassium chloride  
Potassium sulfate  
Sugar  
Urea  
Tungsten ore  
Zinc  
WIENBADEN 1447  
Antimony salts  
Citric acid  
Tartaric acid  
Oxalic acid  
Sodium bisulfate  
Cream of tartar  
Sodium formate  
Potassium oxalate  
Rochelle salt  
Aniline dyes  
Cement  
Fertilizer  
Mineral water  
Stone ware  
Wine

## STATISTICS, ETC., ON EXPORTS TO THE U. S. (PP.)—(Concluded)

HANOVER, 1449  
Ammunition  
Celluloid  
Antimony sulfide  
Arsenic acid  
Creosote  
Mesosborium  
Phosphoric acid  
Thorium nitrate  
Cerium nitrate  
Cobalt  
Glycerine  
Hides  
Infusorial earth  
Inks  
Potash  
Rubber  
Wine  
Wool fat  
ROME—1460  
Aluminum  
Chemicals  
Cork  
Glue stock  
Hides  
Meat extract  
Roses  
Sienna  
BERLIN, GERMANY—  
1544-8  
Glass  
Hides  
Manganese ore  
Scientific instruments  
MOROCCO 1553-62  
Gum sandarac  
BRITISH COLUMBIA—  
1569-80  
Bullion  
Cascara bark  
Fertilizer  
Hides  
Tin  
Wood pulp  
Gold ore  
Zinc ore  
Copper ore  
Blister copper  
Copper matte  
MERSINA, TURKEY  
1601-6  
Gum tragacanth  
Sesame oil and seed  
CHILI 1617-25  
Copper ore  
Iodine  
Sodium nitrate  
Silver ore  
Tin ore  
BERMUS 1655  
Hides  
Mineral wax  
Lac  
Cutch (dye wood)  
Copper matte  
BAHAMAS—1665-72  
Bark  
Hides  
Sisal  
NEWFOUNDLAND—  
1681-90  
Coff oil  
Seal oil  
Whale oil  
Guano  
Iron ore  
Flint pebbles  
GUATEMALA—1714-17  
Hides  
Rubber  
Sugar

Zinc refining in Japan has increased so that not only the domestic demand is supplied, but also some zinc is shipped to England. (P. 1487.)

Annual imports of mineral waters into the United States are over 3,000,000 gallons, valued at \$1,000,000. As these have come principally from Germany, France, and Austria-Hungary, domestic waters will probably soon replace the foreign. The production in this country is about 57,000,000 gallons, valued at \$5,500,000. (P. 1483.)

High-grade iron ore deposits have been discovered on the Copper River, near Hupert, B. C. (P. 1529.)

The peanut and peanut-oil industry of South Carolina are discussed. (P. 1534.)

Tungsten mines in Chosen, Korea are being operated on a small scale. (P. 1549.)

A new pig-iron furnace is to be erected in Chosen, Korea, at a cost of \$2,750,000. (P. 1606.)

The regulations regarding the grading of Manila hemp are discussed. (P. 1607.)

A company has been organized in Ceylon to manufacture sugar from the palmyra palm. (P. 1610.)

A branch laboratory of the Canadian Department of Internal Revenue is to be opened in Vancouver. (P. 1628.)

A plant for making sublimed white lead in Australia is being enlarged. (P. 1628.)

A substitute for ichthyol, to replace the supply from Austria, has been placed on the market. (P. 1675.)

Developments of potash deposits near Barcelona, Spain, have been interrupted by the war. (P. 1717.)

## BOOK REVIEWS

**Chemistry in America:** Chapters from the History of the Science in the United States. By EDGAR FAHS SMITH. New York: D. Appleton and Co. 1914. Pp. xiii + 356. 24 half-tones. Price, \$1.00.

This volume, on the development of chemistry in the United States, may be described rather as a source-book than as a history. It consists largely of biographies of individual chemists, although inter-relations and groupings are not neglected, and the institutions in which chemistry was especially cultivated receive more than incidental mention. The book contains two general addresses, which give an excellent idea of the interests of chemists at the opening of the nineteenth century, and extensive extracts from several original papers.

The earliest contribution to chemistry printed in America seems to be one published in 1768 by John de Normandie.

The balance is frequently mentioned in this paper. It is surely time that the absurd misstatement, to the effect that Lavoisier was the first to use this instrument, should cease to appear in almost every paper and address professing to deal with the history of the science.

It is interesting to note that the Chemical Society of Philadelphia (1792-1809) and its successor, the Columbian Chemical Society, founded in 1811, antedated the European societies devoted to the cultivation of the same science.

The biographical chapters give vivid characterizations of many interesting men. They begin with James Woodhouse, professor of chemistry in the University of Pennsylvania, a vigorous and emphatic personality whose lectures rarely exceeded forty minutes and were often much shorter. Priestley and his relations with American chemists during the last ten years of his life (1794-1804) occupy much space and constitute



one of the most interesting parts of the volume. Thomas Cooper (1759-1841) was probably the first of the large number of chemists who have become college presidents.

The biographies include John Maclean of Princeton, Samuel L. Mitchell of Columbia, Robert Hare of Philadelphia, perhaps the most influential American chemist of his day, and a group of mineralogical chemists headed by Archibald Bruce from whom brucite derives its name.

The concluding part of the volume deals with Guthrie, an independent discoverer of chloroform and the first to use it in medicine, Rogers who experimented in dialysis, T. Sterry Hunt, preeminent as an original thinker, J. Lawrence Smith, Wolcott Gibbs, Mallet, Carey Lea, Cooke of Harvard and Willard Gibbs of Yale.

The work gives an excellent idea of the place of American chemists in the history of chemistry, and we owe a debt of gratitude to the author for publishing the valuable material originally collected for his lectures on the development of the science.

ALEXANDER SMITH

**Chemical Reagents. Their Purity and Tests.** Authorized translation of *Pruefung der Chemischen Reagentien auf Reinheit* (Zweite Auflage) Von E. Merck. By HENRY SCHENCK, A.B. (Harvard). Second edition. 8vo. pp. ix + 199. Cloth. D. Van Nostrand Company, New York. 1914. Price, \$11.00 net.

This latest edition of Merck's Chemical Reagents follows the same general lines as the first edition, which in turn was preceded by the Krauch editions on "*Die Pruefung der Chemischen Reagentien auf Reinheit*," which have appeared successively since 1888. In this edition is appended for the first time a table for the preparation of test solutions commonly used, with general directions and approximate strengths.

The general treatment of the subject matter consists in a brief description of the familiar appearance of the particular reagent, along with detailed tests for the more common impurities. These tests are to be made in the examination, both qualitative and quantitative. In many places are added the use and solubility along with references to such literature as in the author's judgment are the most important new contributions upon the uses and methods of testing reagent chemicals. This listing of references is of particular value to the analytical chemist who is frequently called upon to make a more elaborate examination of his reagents than is described in the ordinary manual. In this connection it is noted, however, that under Sodium Oxalate (Soerensen's Oxalate) the valuable work of Blum of the U. S. Bureau of Standards, one of the most elaborate investigations on a chemical reagent, is not mentioned. It is possible that inasmuch as this work was published in 1912, the translator overlooked this important article. It is to be noted that the Tests of Purity applied to oxalic acid and the oxalates do not call attention to calcium which is so likely to be present.

On the whole this standard handbook treats the testing of the more common reagents in a highly satisfactory manner for a small book and it is gratifying to know that frequent editions of this valuable manual appear from time to time.

VICTOR LENHER

**Sammlung Vieweg, Heft 2. Anorganische Peroxyde und Persalze.** By DR. C. FREIHERRN VON GIRSEWALD. 98 pp. Paper, M. 2.40. **Heft 6. Brennerfragen.** By D. SIDERSKY. Illustrated. 49 pp. Paper, M. 1.60. Friedr. Vieweg & Sohn, Braunschweig, 1914.

These two recently issued books are among the first six volumes issued of the "*Sammlung Vieweg*," a collection which, it is planned, shall cover all the branches of pure and applied science and shall present in each subject its strictly contemporaneous state of development.

Dr. von Girssewald has divided the main part of his book into two divisions, one dealing with hydrogen peroxide and the other with derivatives such as the true metal peroxides, persalts like the perborates, etc. While the theoretical part of the subject is not neglected, the chief interest of the book is in the development of the practical applications of peroxides to industry.

In the theoretical part the discussion of the formula of hydrogen peroxide (that preferred by the author is  $H-O-O-H$ ) is not always thoroughly convincing and it appears a mistake to insist so strongly on any detailed structural formula.

The book is on the whole interesting and instructive, and the author is to be commended for introducing the necessary feature—sometimes omitted in such books—of profuse references to original sources, especially patent literature; the work is sufficiently exhaustive to give a true picture of the present-day status of peroxides and persalts, as well as point out the probable lines of future development.

"*Brennerfragen*" deals with the questions of modern, chiefly French and Austrian, distilling practice. The first part treats of the continuous fermentation of beet juice (the chief source of spirits in France and Austria as opposed to Germany where potatoes and grain are the commonest raw materials), while the second part takes up distillation and rectification. The book is well illustrated with microphotographs and many pictures and diagrams of apparatus.

M. L. HAMLIN

**Rapid Method for the Chemical Analysis of Special Steels, Steel-Making Alloys, and Graphite.** By CHARLES MORRIS JOHNSON, Ph.M., Chief Chemist to the Park Steel Works of the Crucible Steel Co. of America. Second edition. xi + 437 pages, 39 figures. John Wiley & Sons, Inc., New York. Price, \$3.00 net.

The first edition of Mr. Johnson's book, published in 1909, met with a hearty reception and a ready sale to those who were interested in alloy steels. An important feature of the first edition was the incorporation of methods of analysis of alloy steels, wherein the author gave actual methods used in control work of operations. The methods were based on experimental data covering years of experience.

In the introduction to the second edition special attention is called to the following general statement: "If iron be combined by fusion with notable quantities of an element whose melting point is very much below that of iron, the tendency is to produce a metal of inferior physical properties, but if iron be combined with an element whose melting point is nearly that or higher than that of iron, then the tendency is to produce a metal of superior physical properties."

Attention is also called to the author's methods for the determination of phosphorus in tungsten-bearing materials; tungsten in ores; for sulfur in alloy steels by heating the insoluble carbides, which carry the major part of the sulfur, to a yellow heat in a stream of acid-carrying hydrogen, evolving the sulfur as hydrogen sulfide from sulfates; modification of Brunk's method for nickel in steel; the titration of iron or vanadium or both in the presence of uranium; uranium in ores; ferro uranium and steels; cobalt steels and cobalt metals; to the author's investigation of the cause of bark in pipe-annealed steel, tapered clay combustion tubes, milling machine, one piece nichrome triangle, and the plan and views of laboratory rooms.

The second edition is enlarged, the author elaborating on methods given in the first edition. He has also added new methods based on more recent experience, and has brought the book up to the latest and best analytical practice in iron, steel and its alloys. Additional chapters give methods for the testing of lubricating oils, coal, iron ore, fluorspar, limestone, sand and brick. The aim of the author has been to produce methods that combine speed, simplicity and accuracy.

WILLIAM BRADY

## NEW PUBLICATIONS

By JOHN F. NORTON, Massachusetts Institute of Technology, Boston

- Air: Pumping by Compressed Air.** By E. M. IVENS. 8vo. 244 pp. Price, \$4.00. John Wiley & Sons, New York.
- Analysis: Chemical Analysis, Qualitative and Quantitative.** By G. I. GARDNER. 8vo. 501 pp. Price, \$4.00. Black, London.
- Analysis: Introduction to Qualitative Chemical Analysis (Anleitung zur qualitativen chemischen Analyse).** By H. V. PICHMANN. 14th Ed. by W. Brandt. 8vo. 138 pp. Price, \$0.50. Munich (German).
- Analysis: Principles of Quantitative Analysis: An Introductory Course.** By W. C. BLANCKE. 12mo. 394 pp. Price, \$2.50. D. Van Nostrand Co., New York.
- Analysis: Tables for Qualitative Chemical Analysis, (Tafeln für qualitativen chemischen Analyse).** By H. V. PICHMANN. 14th Ed. by W. Brandt. 8vo. 39 pp. Price, \$0.35. Munich. (German.)
- Analysis: Technical Methods of Ore Analysis.** By ALBERT H. LOW. 6th Ed. 8vo. 362 pp. Price, \$2.75. John Wiley & Sons, New York.
- Brewing: The Modern Brewery. A Practical Handbook for the Brewer (Die Bierbrauerei der Neuzeit).** By S. ZIMMERMANN. 8vo. Price, \$2.50. Bartenstein. (German.)
- Experiments.** By PHILIP E. EDELMAN. 250 pp. Price, \$1.50. Philip E. Edelman, Minneapolis, Minn.
- Food: Foods and Sanitation, a Text-book and Laboratory Manual for High Schools.** By EDITH H. FORSTER and MILDRED WIGLEY. 12mo. 396 pp. Price, \$1.00. Row, Peterson & Co., Chicago.
- General Chemistry: Foundations of Chemistry.** By ARTHUR A. BLANCHARD and F. B. WADE. 12mo. 446 pp. Price, \$1.25. American Book Co., New York.
- General Chemistry: Laboratory Experiments in General Chemistry.** By H. B. NORTH. 2nd Ed., revised. 12mo. 205 pp. Price, \$1.00. D. Van Nostrand Co., New York.
- Household Chemistry: Elementary Household Chemistry.** By JOHN F. SNELL. 12mo. 307 pp. Price, \$1.25. The Macmillan Co., New York.
- Inorganic Chemistry: Text Book of Inorganic Chemistry.** By A. F. HOLLEMAN. 12th Ed. 8vo. Price, \$2.00. Leipzig. (German.)
- Inorganic Chemistry: The Principles of Inorganic Chemistry.** By WILHELM OSTWALD. Translated by Alex. Findlay. 4th Ed. 8vo. 836 pp. Price, \$4.50. The Macmillan Co., New York.
- Iron: Iron Ores, their Occurrence, Valuation\* and Control.** By E. C. ECKEL. 8vo. 427 pp. Price, \$4.00. McGraw-Hill Book Co., New York.
- Oils: Mineral Oils and Their By-products.** By ILTYD I. REDWOOD. 2nd Ed. 8vo. 336 pp. Price, \$3.00. Spon & Co., New York.
- Oils: The Hydrogenation of Oils: Catalysts and Catalysis; and the Generation of Hydrogen.** By CARLETON ELLIS. 8vo. Price, \$4.00. D. Van Nostrand Co., New York.
- Physical Chemistry: A Manual of Practical Physical Chemistry.** By F. W. GRAY. 12mo. 211 pp. Price, \$1.25. The Macmillan Co., New York.
- Physical Chemistry: Hydrogen Ion Concentrations. (Die Wasserstoffionen-Konzentration.)** By L. MICHAELIS. 8vo. 210 pp. Price, \$2.00. J. Springer, Berlin. (German.)
- Physiology: A Text-Book of Physiological Chemistry.** By OLOF HAMMARSTEN. Translation by John A. Mandel. 7th Ed., English. 8vo. 1014 pp. Price, \$4.00. John Wiley & Sons, Inc., New York.
- Rubber: The Rubber Industry in Brazil and the Orient.** By C. E. AKERS. 8vo. 33 pp. Price, \$1.50. Methuen, London.
- Tanning: Handbook for Tannery Laboratories (Handbuch fuer gerberei-chemische Laboratorien).** By G. GRASSER. 8vo. 395 pp. Price, \$4.00. Schulze & Co., Leipzig. (German.)
- Textiles: The Chemical Technology of Spun Yarn (Chemische Technologie der Gespinnstfasern).** By K. STERN. Price, \$3.50. Borntraeger Berlin. (German.)
- Tipplate: The Tipplate Industry. With Special Reference to Its Relations with the Iron and Steel Industries.** By J. H. JONES. 8vo. 302 pp. Price, \$2.00. P. S. Kink, London.
- Welding: A Practical Manual of Autogenous Welding (Oxy-Acetylene).** By R. GRANSON and P. ROSEMBERG. 8vo. 256 pp. Price, \$1.25. C. Griffin, London.
- Wines: Faults and Diseases of Wines, Their Causes, Recognition, and Remedies. (Fehler und Krankheiten des Weines, deren Ursachen, Erkennung und Heilung.)** By J. L. MERZ. 8vo. 108 pp. Price, \$0.75. Wien. (German.)
- Analysis: The Perchloric Method of Determining Potassium, as Applied to Water Analysis.** By CLARENCE SCHOLL. *Journal of the American Chemical Society*, Vol. 36, 1914, No. 10, pp. 3085-88.
- Carbon: Energy of Vaporization of Carbon.** By CARL HERRING. *Metallurgical and Chemical Engineering*, Vol. 12, 1914, No. 8, pp. 526-8.
- Colloids: The Theory of Colloid Chemistry.** By WILDER D. BANCROFT. *The Journal of Physical Chemistry*, Vol. 18, 1914, No. 7, pp. 549-58.
- Combustion: Coal Flames with Ether.** By ALAN LEIGHTON. *The Journal of Physical Chemistry*, Vol. 18, 1914, No. 7, pp. 619-23.
- Combustion: Surface Combustion.** By W. A. BONS. *The Chemical Engineer*, Vol. 20, 1914, No. 3, pp. 99-109.
- Creosote: Efficiency of Various Parts of Coal-Tar Creosote against Marine Borers.** By CLYDE H. TRESDALE. *Engineering Record*, Vol. 70, 1914, No. 11, pp. 302-3.
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- Textiles: Oils and Soaps Used in Textile Manufacturing.** ANONYMOUS. *The Textile American*, Vol. 22, 1914, No. 3, pp. 34-6.
- Tungsten, Studies on the Analytical Examination of.** By HANS ARNOLD. *Zeitschrift fuer anorganische Chemie*, Vol. 88, 1914, No. 3, pp. 333-340.
- Turpentine, Detection and Determination of, Petroleum Derivatives in.** By C. GRUNALDI and L. PRUSSIG. *Chemiker Zeitung*, Vol. 38, 1914, No. 95, pp. 1001-1002.
- Water: Applications of Water Analysis.** By EDWARD BARTOW. *American Journal of Public Health*, Vol. 4, 1914, No. 8, pp. 633-37.
- Water: Conservation of Potable Water and the Dual System of Distribution.** By HENRY C. HODGKINS. *Journal of the American Water Works Association*, Vol. 1, 1914, No. 3, pp. 554-64.
- Water: Disinfecting 200,000,000 Gallons of Water a Day—Experience with Chloride of Lime and Liquid Chlorine.** By FRANCIS D. WEST. *Journal of the American Water Works Association*, Vol. 1, 1914, No. 3, pp. 403-55.

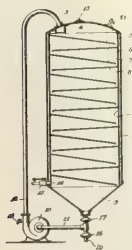
## RECENT JOURNAL ARTICLES

- Analysis: Improved Apparatus for the Analysis of Mixed Gases.** By A. C. WILSON. *The Analyst*, Vol. 39, 1914, No. 462, pp. 391-2.
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# RECENT INVENTIONS

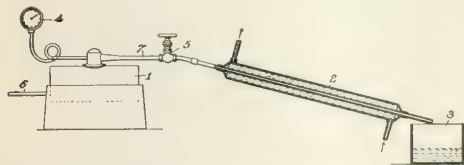
By C. L. PARKER, Solicitor of Chemical Patents, McGill Building, Washington, D. C.

**Hydrogenating Oils, Fats, and Fatty Acids, Etc.** J. N. Humphreys, June 23, 1914. U. S. Pat. 1,100,735. The oil to be hydrogenated is mixed with a finely divided catalytic agent and caused to move in a film relatively slowly and quietly over a circuitous path in an atmosphere containing hydrogen.



**Treatment of Petroleum Hydrocarbons.** Bacon and Clark, June 23, 1914. U. S. Pat. 1,101,482. This process is designed for converting into gasoline petroleum hydrocarbons from which the usual gasoline content has already been removed by fractional distillation or hydrocarbons normally free from gasoline.

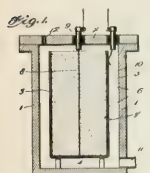
The process consists in producing saturated gasoline hydrocarbons (*i. e.*, hydrocarbons having boiling points ranging from about 30° C. to 150° C., at atmospheric pressure), by simultaneously decomposing and distilling under a pressure of from 100 to 300 pounds per sq. in. petroleum hydrocarbons having a boil-



ing point of about 250° C. and upward, the operation being continued at a rate to give a yield of saturated gasoline hydrocarbons of a minimum volume of 18 per cent of the distilling charge, and subsequently treating the distillate thus obtained for the separation of the saturated gasoline hydrocarbons.

**Carbon-Remover.** C. B. Longenecker, June 30, 1914. U. S. Pat. 1,101,646. This is a compound for treating cylinders of internal combustion engines consisting of sodium chlorid and sulfur.

**Sulfur and Sulfates from Sulfitcs.** C. Hansen, June 30, 1914. U. S. Pat. 1,101,740. Sulfur and sulfates are produced by heating solutions of a mixture of two molecules of a bisulfite with one molecule of a sulfite under pressure and with continuous stirring.

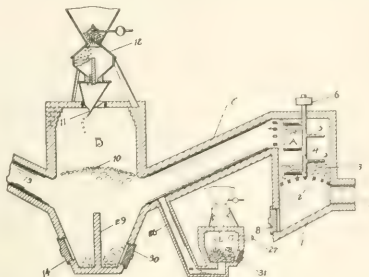


**Method and Means for Fixing Nitrogen.** W. S. Landis, July 14, 1914. U. S. Pat. 1,103,060 and 1,103,062. Calcium carbide contained within a bag of loosely woven fabric is placed within porous vessel 3 in the chamber 1 and electrically heated, nitrogen being admitted through pipe 11 during the heating operation.

**Fertilizer.** F. S. Washburn, July 14, 1914. U. S. Pat. 1,103,115. The phosphoric acid contained in phosphate rock is rendered available as a plant food by treating the rock with sulfuric acid to obtain a crude solution of phosphoric acid and then feeding the crude solution so obtained to a solution containing di-ammonium phosphate.

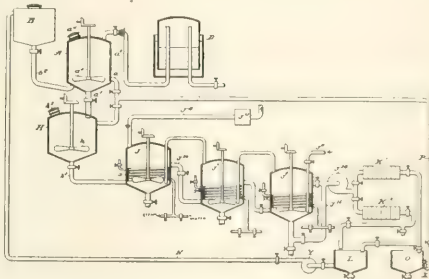
**Rendering Smelter Fumes Useful and Recovery of Their Values.** C. S. Vadner, July 14, 1914. U. S. Pat. 1,103,165. The smelter fumes are purified of their mechanical impurities by passing them through the mechanical filter in the chamber

"A." They are then mixed with hydrocarbon gases and the mixture heated to a high temperature in the gas converting chamber "B," thereby rearranging them in their combinations.



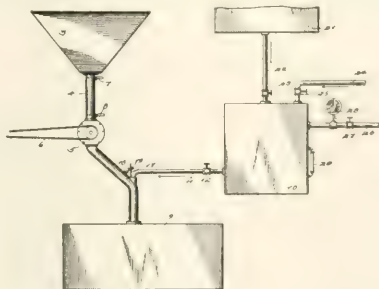
Combustible gases in the remaining mixture are recovered by cooling, whereby part of the impurities and the moisture are eliminated.

**Process of Making Bisulfite of Soda.** H. Howard, July 28, 1914. U. S. Pat. 1,104,897. Lime-mud is reacted upon with sodium bisulfite, thereby forming calcium sulfite and sodium



sulfite. Sodium sulfate is added and the resulting mixture is reacted upon with sulfur dioxide at a temperature between 45° C. and 65° C., thereby forming calcium sulfate and sodium bisulfite.

**Calcium Acid Phosphate.** E. W. Reed, July 28, 1914. U. S. Pat. 1,105,304. A moving body of air laden with the finely



divided phosphate material to be transformed into calcium acid phosphate is sprayed with sulfuric acid, the process being preferably carried out in the apparatus illustrated.



# MARKET REPORT

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR THE MONTH OF OCTOBER, 1914

## ORGANIC CHEMICALS

Acetanilid.....	Lb.	30	@	32
Acetic Acid (28 per cent).....	C.	1.50	@	1.65
Acetone (drums).....	Lb.	11 1/2	@	12 1/2
Alcohol, denatured (180 proof).....	Gal.	33	@	35
Alcohol, grain (188 proof).....	Gal.	2 60	@	2 65
Alcohol, wood (95 per cent).....	Gal.	45	@	47
Amyl Acetone.....	Gal.	2 50	@	2 75
Aniline Oil.....	Lb.	—	@	—
Benzoic Acid.....	Lb.	—	@	—
Benzol (90 per cent).....	Gal.	—	@	—
Camphor (refined in bulk).....	Lb.	—	@	60
Carbolic Acid (drums).....	Lb.	36	@	38
Carbon Bisulfide.....	Lb.	10	@	15
Carbon Tetrachloride (drums).....	Lb.	—	@	15
Chloroform.....	Lb.	30	@	35
Citric Acid (domestic), crystals.....	Lb.	70	@	72
Dextrine (corn).....	C.	3 07	@	3 32
Dextrine (imported potato).....	Lb.	—	@	—
Ether (U. S. P., 1900).....	Lb.	15	@	20
Formaldehyde.....	Lb.	8 1/2	@	9 1/2
Glycerine (dynamite).....	Lb.	24	@	25
Oxalic Acid.....	Lb.	15	@	18
Pyrogallie Acid (bulk).....	Lb.	1 90	@	2 10
Salicylic Acid.....	Lb.	1 20	@	1 25
Starch (cassava).....	Lb.	3 1/4	@	4
Starch (corn).....	C.	2 39	@	2 50
Starch (potato).....	Lb.	—	@	—
Starch (rice).....	Lb.	—	@	—
Starch (sago).....	Lb.	—	@	—
Starch (wheat).....	Lb.	5	@	10
Tannic Acid (commercial).....	Lb.	60	@	66
Tartaric Acid, crystals.....	Lb.	50	@	55

## INORGANIC CHEMICALS

Acetate of Lead (brown, broken).....	Lb.	7 1/4	@	7 1/2
Acetate of Lime (gray).....	C.	1.50	@	1.55
Alum (lump).....	C.	2.75	@	3.00
Aluminum Sulfate (high-grade).....	C.	1.50	@	2.00
Ammonium Carbonate, (domestic).....	Lb.	10	@	11
Ammonium Chloride, (gray).....	Lb.	6 1/4	@	6 1/4
Aqua Ammonia (drums) 16°.....	Lb.	2 1/4	@	2 1/2
Arsenic (white).....	Lb.	5	@	6
Barium Chloride.....	Ton	1 20	@	1 30
Barium Nitrate.....	Lb.	—	@	—
Barytes (prime white, foreign).....	Ton	20 00	@	27 00
Bleaching Powder (35 per cent).....	C.	2 00	@	3 00
Blue Vitriol.....	C.	4 50	@	4 75
Borax, crystals (bags).....	Lb.	3 1/4	@	4 1/2
Boric Acid, crystals (powd.).....	Lb.	7 1/4	@	8
Brimstone (crude, domestic).....	Long Ton	22 00	@	22 50
Bromine (bulk).....	Lb.	40	@	50
Calcium Chloride (lump).....	Ton	11 80	@	12 00
Chalk (light precipitated).....	Lb.	8	@	10
China Clay (imported).....	Ton	14 00	@	16 00
Feldspar.....	Ton	—	@	—
Fuller's Earth (powdered, foreign).....	Ton	—	@	—
Green Vitriol (bulk).....	C.	55	@	60
Hydrochloric Acid (18°).....	C.	1 15	@	1 65
Iodine (resublimed).....	Lb.	3 75	@	4 00
Lead Nitrate.....	Lb.	8 1/4	@	8 1/2
Litharge (American).....	Lb.	5	@	5 1/4
Lithium Carbonate.....	Lb.	1 25	@	1 30
Magnesium Carbonate.....	Lb.	5	@	6
Magnesite "Calined".....	Ton	45 00	@	50 00
Nitric Acid (36°).....	Lb.	3 1/4	@	4 1/4
Phosphoric Acid (sp. gr. 1.75).....	Lb.	28	@	28 1/2
Phosphorus.....	Lb.	35	@	95
Plaster of Paris.....	Bbl.	1 50	@	1 70
Potassium Bichromate (50°).....	Lb.	13	@	15
Potassium Bromide.....	Lb.	70	@	80
Potassium Carbonate (calined), 80 @ 85°.....	C.	12	@	15
Potassium Chlorate, crystals.....	Lb.	15	@	16
Potassium Cyanide (bulk), 98-99%.....	Lb.	25	@	30
Potassium Hydroxide.....	C.	3 00	@	40 00
Potassium Iodide (bulk).....	Lb.	3 15	@	3 25
Potassium Nitrate (crude).....	Lb.	—	@	—
Potassium Permanganate (bulk).....	Lb.	35	@	40
Quicksilver, Flask (75 lbs.).....	50.00	@		
Red Lead (American).....	Lb.	5 1/2	@	6
Salt Cake (glass makers').....	C.	55	@	65

Silver Nitrate.....	Oz.	33	@	35
Soapstone in bags.....	Ton	10 00	@	12 00
Soda Ash (48 per cent).....	C.	67 1/2	@	72 1/2
Sodium Acetate.....	Lb.	5	@	7
Sodium Bicarbonate (domestic).....	C.	1 00	@	1 10
Sodium Bicarbonate (English).....	Lb.	3 1/2	@	4
Sodium Bichromate.....	Lb.	4 1/2	@	5
Sodium Carbonate (dry).....	C.	60	@	80
Sodium Chloride.....	Lb.	—	@	14
Sodium Hydroxide (60 per cent).....	C.	1 55	@	1 57 1/2
Sodium Hyposulfite.....	C.	1 60	@	1 90
Sodium Nitrate (95 per cent, spot).....	C.	—	@	1 90
Sodium Silicate (liquid).....	C.	60	@	70
Strontium Nitrate.....	Lb.	15	@	17
Sulfur, Flowers (sublimed).....	C.	2 20	@	2 60
Sulfur, Roll.....	C.	1 85	@	2 15
Sulfuric Acid (60° B).....	C.	85	@	1 00
Talc (American).....	Ton	15 00	@	20 00
Terra Alba (American), No. 1.....	C.	75	@	80
Tin Bichloride (50°).....	Lb.	99 1/4	@	10
Tin Oxide.....	Lb.	37	@	38
White Lead (American, dry).....	Lb.	5 1/2	@	5 1/2
Zinc Carbonate.....	Lb.	8 1/2	@	9
Zinc Chloride (granulated).....	Lb.	4 1/2	@	5
Zinc Oxide (American process).....	Lb.	5 1/2	@	6 1/2
Zinc Sulfate.....	C.	2 35	@	2 70

## OILS, WAXES, ETC.

Beeswax (pure white).....	Lb.	45	@	57
Black Mineral Oil, 29 gravity.....	Gal.	13 1/2	@	14
Castor Oil (No. 3).....	Lb.	8 1/4	@	9
Ceresin (yellow).....	Lb.	12	@	22
Corn Oil.....	C.	5 45	@	5 55
Cottonseed Oil (crude), f. o. b. mill.....	Gal.	29	@	30
Cottonseed Oil (p. s. y.).....	Lb.	51 1/2	@	6
Cylinder Oil (light, filtered).....	Gal.	21 1/2	@	32
Japan Wax.....	Lb.	13	@	14
Lard Oil (prime winter).....	Gal.	90	@	92
Linseed Oil (raw).....	Gal.	45	@	50
Menhaden Oil (crude).....	Gal.	33	@	—
Neatsfoot Oil (20°).....	Gal.	96	@	98
Paraffine (crude, 120 & 122 m. p.).....	Lb.	3 1/4	@	3 1/4
Paraffine Oil (high viscosity).....	Gal.	27	@	28
Rosin ("P" grade) (280 lbs.).....	Bbl.	4 05	@	—
Rosin Oil (first run).....	Gal.	25	@	—
Shellac, T. N.....	Lb.	17	@	18
Spermaceti (cake).....	Lb.	28	@	30
Sperm Oil (bleached winter), 38°.....	Gal.	70	@	71
Spindle Oil, No. 200.....	Gal.	18	@	19
Stearic Acid (double-pressed).....	Lb.	9	@	11
Tallow (acidless).....	Gal.	64	@	66
Tar Oil (distilled).....	Gal.	30	@	31
Turpentine (spirits of).....	Gal.	47 1/2	@	48

## METALS

Aluminum (No. 1 ingots).....	Lb.	18	@	18 1/2
Antimony (Hallet's).....	Lb.	12	@	12 1/2
Bismuth (New York).....	Lb.	2 10	@	2 15
Bronze powder.....	Lb.	—	@	—
Copper (electrolytic).....	C.	11 15	@	—
Copper (lake).....	C.	11 67 1/2	@	—
Lead, N. Y.....	C.	3 50	@	—
Nickel.....	Lb.	—	@	—
Platinum (refined).....	Oz.	50 00	@	52 00
Silver.....	Oz.	50 1/2	@	—
Tin.....	C.	28 75	@	30 00
Zinc.....	C.	4 80	@	4 90

## FERTILIZER MATERIALS

Ammonium Sulfate.....	C.	2 55	@	2 62 1/2
Blood (dried).....	Unit	3 15	@	3 20
Bone, 4 1/2 and 50 (ground, raw).....	Ton	27 50	@	—
Calcium Cyanamid.....	Unit of Ammonia	2 22 1/2	@	2 40
Calcium Nitrate (Norwegian).....	C.	—	@	—
Castor meal.....	Unit	—	@	—
Fish Scrap (domestic, dried).....	Unit	3 00	@	10
Phosphate, acid (16 per cent bulk).....	Ton	7 50	@	—
Phosphate rock; f. o. b. mine.....	Ton	2 25	@	2 50
Florida land pebble (68 per cent).....	Ton	5 00	@	5 50
Tennessee (70-80 per cent).....	Ton	—	@	—
Potassium, "muriate," basis 80 per cent.....	Ton	—	@	nominal
Pyrites (furnace size, imported).....	Unit	13	@	—
Tankage (high-grade).....	Unit	3 15	@	10

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## TABLE OF CONTENTS

### EDITORIALS:

Analysis of the Coal-tar Dye Industry.....	972
Recommendations of the New York Section of the American Chemical Society on the Enlargement of the Coal-tar Chemical Industry in the United States.....	972

### ORIGINAL PAPERS:

The Cementing Value of Bituminous Binders. By Lester Kirschbraun.....	976
Hysteresis Tests for Rubber. By Earle L. Davies....	985
A Study of the Efficiency of Various Methods for the Filtration of Sugar Solutions. By Alfred E. Roberts.....	986
The Absorption of Gasoline Vapor in Natural Gas by Fuming Sulfuric Acid. By R. P. Anderson and C. J. Engelder.....	989
The Determination of Hydrogen in Gas Mixtures by Means of Colloidal Palladium. By G. A. Burrell and G. G. Oberfell.....	992
Iodine Number of Linseed and Petroleum Oils. By W. H. Smith and J. B. Tuttle.....	994
Egg Albumin in Baking Powder. By H. Louis Jackson.....	998
Iron in Tomatoes. By C. A. Brautlecht and G. Crawford.....	1001
Blood-Charcoal as a Purifying Agent for Arsenic Solutions Previous to Titration. By Robert M. Chapin.....	1002
The Strength of Nitric Acid, Period of Extraction, and Ignition as Affecting the Gravimetric Determination of Phosphoric Acid in Soils. By O. L. Brauer.....	1004
Comparison of Silicates and Carbonates as Sources of Lime and Magnesia for Plants. By W. H. MacIntire and L. G. Willis.....	1005
A Simple Method for Determining the Critical Moisture Content of Soils. By R. O. E. Davis.....	1008

### LABORATORY AND PLANT:

A New and Improved Form of Kjeldahl Distillation Apparatus. By Arthur D. Holmes.....	1010
A Convenient Color Camera. By C. M. Clark.....	1012
Improved Method for the Determination of Nitrogen in Steel. By L. E. Barton.....	1012

### ADDRESSES:

The Industry of the Coal-Tar Dyes. An Outline Sketch. By Bernhard C. Hesse.....	1013
Gas Manufacture from the Point of View of Physical Chemistry. By W. F. Rittman.....	1027
The Broader Applications of Chemistry by the Municipality. By Hermann W. Mahr.....	1030

### CURRENT INDUSTRIAL NEWS:

Instruments for Testing Gas.....	1032
The Impermeability of Concrete.....	1033
Putting Electrotyping Industry on More Scientific Basis.....	1033
The Balance of Trade in Chemicals between the United States and Germany in 1913.....	1034

### NOTES AND CORRESPONDENCE:

Strontium in the Beet Sugar Industry.....	1036
The Effect of Steam upon Magnesite Brick or Calcined Magnesite.....	1037
Conversion Table for Glues.....	1037
Cap for Bunsen Burner Used with Natural Gas.....	1037
A Shaker for the Mechanical Analysis of Soils—Note.....	1038
American Institute of Chemical Engineers, 7th Annual Meeting, Philadelphia, December 2-5, 1914.....	1038
Communication from the Analytical Committee, Rubber Section, American Chemical Society.....	1038
The Specific Heat of California Petroleum—A Correction .....	1039
The Explosibility of Grain Dusts—A Correction.....	1039

### PERSONAL NOTES.....

### GOVERNMENT PUBLICATIONS.....

BOOK REVIEWS: Industrial Chemistry for Engineering Students; Metallurgy of Copper; Fixation of Atmospheric Nitrogen; Neues Handbuch der Chemischen Technologie; Examination of Lubricating Oils; Laboratory Course in Electrochemistry; Chemistry of Rubber; A Chart of the Carbon Compounds.....	1045
---	------

### NEW PUBLICATIONS.....

### RECENT INVENTIONS.....

### MARKET REPORT.....

### AUTHOR INDEX.....

### SUBJECT INDEX.....

## EDITORIALS

### ANALYSIS OF THE COAL-TAR DYE INDUSTRY

We are pleased to publish in this issue a lecture on the Coal-Tar Dye Industry which was presented at a meeting of the Board of Directors of the General Chemical Company, on October 23rd, by Dr. Bernhard C. Hesse. This comprehensive analysis of the problem is of peculiar interest at the present time on account of the numerous articles appearing in the daily and magazine press, calling upon the chemical manufacturers of America for the immediate establishment of plants for the production of coal-tar dyes, to prevent a shortage of these products on account of the European war.

It is generally assumed, and often stated, that the United States is not a factor in the coal-tar dye industry because of lack of enterprise or skill on the part of our chemists and chemical manufacturers, but this is far from the truth.

The complexity of this industry is but little understood by the layman. We believe that the careful analysis of the problem which Dr. Hesse has made for the men responsible for the policies of a great chemical manufacturing company will be read with interest and profit, not only by the men charged with the responsibility of developing chemical industry, but by the public who are entitled to know why the hue and cry of the superficial hack-writer is not answered by the immediate erection of great coal tar dye factories. Industrial development, more especially in the case of the coal-tar dye industry, is dependent for its success upon a large number of conditions entirely independent of the financial investment or the technical skill involved in the operation of the processes. An analysis of the charts used to illustrate the lecture shows at a glance the intricate complications of the technical features of coal-tar dye production. These complications do not present insurmountable technical obstacles to the American manufacturer. A more thorough analysis of the lecture and the charts, however, brings out many important points not usually considered. There is the intimate interlocking of processes and products in which an economic balance must be maintained or some phase of the operation will be required to carry prohibitive cost burdens. The slightest change in the value of an intermediate by-product from one of the operations may serve to upset this economic balance, and thereby change the whole process of manufacture. This point is particularly well illustrated in the manufacture of indigo and the influence of the by-products in determining the raw material, process and plant which is used.

The patent situation, which is frequently referred to as being a controlling factor in the German domination of the dye industry, is shown by Dr. Hesse to be deserving of very little consideration, as both the process and product patents have expired in the case of a large number of the important products. On the other hand, the influence of the tariff on the development of

this industry is carefully discussed. The important point is made, which has frequently been suggested in connection with other developments, that the attitude of the consumers of these products in regard to tariff increases is conducive to the development of these industries abroad, rather than in our own country. When consumers prevent proper tariff protection on products which are or could be manufactured at home, it invariably results in fostering the interests of foreign competitors.

America can have a coal-tar dye industry if she pays the price. Dr. Hesse has clearly set forth the conditions which must be met to make possible the development of the industry in the United States. Such an undertaking means that we are attacking the most favorably situated and strongly fortified industrial position in the manufacturing world. In Germany the coal-tar dye production is geographically centralized in relation to the required raw products; it is the most complicated technical and commercial industry known; it is Germany's most prized and profitable industry; the economic balance of by-products which makes their industry possible would not hold in the United States, and years would be required for the up-building of a corresponding industry here.

Obviously the development of an American dyestuff industry will require for its establishment every known condition which can favor success. The unlimited support and cooperation of the consumer, the public and the government would be a small price to pay to compensate the manufacturer who has the resources, the courage and the skill to undertake the herculean task of developing a coal-tar dye industry in cooperation or in competition with Germany.

### RECOMMENDATIONS OF THE NEW YORK SECTION OF THE AMERICAN CHEMICAL SOCIETY ON THE ENLARGEMENT OF THE COAL TAR CHEMICAL INDUSTRY IN THE UNITED STATES

The special committee appointed by the New York chemists to investigate and report upon conditions and needs involved in the enlargement of the coal tar dye industry in the United States reported at the regular stated meeting of the New York Section of the American Chemical Society on November 6th. The meeting had been widely advertised and was unusually well attended.

This committee was composed of the following members: J. B. F. Herreshoff, representing the manufacturers of heavy chemicals; I. F. Stone, representing the American coal tar dye producers; J. Merritt Matthews, representing the textile interests; H. A. Metz, representing the importers; David W. Jayne, representing the producers of crude coal tar products; Allen Rogers, Chairman of the New York Section; and Bernhard C. Hesse, chemical expert in coal tar dyes, *Chairman*.

The findings of this committee were considered in



detail and after discussion the report was unanimously adopted by the Section and ordered printed in THIS JOURNAL.

In view of the importance of these recommendations, and the highly representative character of the committee, their conclusions will doubtless be of the greatest value not only to the chemical profession, but also to the layman interested in our industrial possibilities.

The following is the official text of the report:

TO THE NEW YORK SECTION, AMERICAN CHEMICAL SOCIETY:

I—At the meeting on October 9, 1914, the chairman of this Section was authorized to appoint a committee to investigate into the feasibility of expanding the chemical and dyestuff industry in the United States and to report to the Section on November 6, 1914.

2—The undersigned committee was appointed October 15th, and at once proceeded. It addressed letters of invitation to cooperate to those who have been most active in the public prints in urging the expansion of the chemical and particularly the dyestuff industry in the United States; further, an invitation was extended to the maker of the motion which resulted in the appointment of this committee. The assistance from these is *nil*.

3—A request was addressed to trade publications in the City of New York and to some of the metropolitan dailies; in all, nine such publications were requested to publish a suggested notice for the purpose of inviting cooperation; the object of this committee was set forth, and request was made that suggestions be mailed to the chairman of this committee. All but one of these publications have complied with that request. No help has been obtained by this committee from any suggestions mailed to it as a result of this publicity.

4—Your committee has carefully considered all the public suggestions as to methods of improvement and has searched through the governmental regulations of the belligerent nations as to embargo and as to contraband of war in order to construct therefrom a list of chemicals, inclusive of dyestuffs, which have thereby been shut off from the United States, in the hope of thus being placed in a position to make specific recommendations of value.

5—It can be fairly stated that, in general, the chemical industry of this country is efficiently exploited and is making full use of all the opportunities presented to it under the normal conditions existing prior to the state of hostilities. Some of the chemicals which are imported from abroad are made in considerable amounts in this country as well, and the amounts imported under normal conditions depend upon the ordinary normal fluctuations of business conditions both here and abroad. With the stoppage of this foreign supply the domestic production was not at once capable of making up the deficiency, but in a number of instances the American manufacturers have taken steps to increase their capacity, and the strain in the market of those particular things will exist no longer than it will require to expand the manufacturing facilities to the proper extent.

Among these are: ammonia salts, barium chloride, barium nitrate, bleaching powder, sodium cyanide, yellow prussiate, sodium nitrate, sodium hydrosulfite, zinc dust.

6—If, however, it be desired, and if public necessity requires the introduction of the manufacture of explosives and further chemicals and dyestuffs into our home industry, such as coal-tar product explosives, pharmaceuticals, medicinals and other intermediates and finished coal-tar dyes, then alterations of our tariff law are inevitable, and the consumers in the first place and the public in general must share in the burden thus imposed. If conditions of national defense in case of attack by a foreign power require us to manufacture our own explosives and to be, in that regard, independent of all foreign nations at all times,

or if our textile industries or any other of our industries requiring coal-tar chemicals such as dyestuffs shall forever be protected and made independent of foreign nations for the supply of those materials, then the nation as a whole must bear the burden incident to such expansion. Under existing circumstances private enterprise and private capital have gone their limit. They have reached the limit for two reasons:

I—The explosive, dye and similar industries abroad, just referred to, are in a state of high development and of refined organization and are financially the best suited to carry on an offensive campaign against any nation attempting to take business away from them.

II—Domestic manufacturers are prohibited by law from making use of cooperative commercial devices such as pools, trusts, manufacturing and selling agreements and the like, whereas such devices are wholly lawful abroad and are encouraged by the respective governments. In other words, the American chemical industry is expected to cope with the foreign industry while both its own arms are tied behind its back and its opponents have full and free use of their arms.

#### ANTI-DUMPING CLAUSE

7—The remedies required would include an effective anti-dumping clause that would certainly prevent underselling of domestic manufacturers in the United States by unfair methods. What the form of such clause should be is a problem with which your committee is unable to cope; it is strictly a law-making and law-enforcing problem and is allied to the usual problem of determining under-valuation as heretofore carried on by our Treasury Department; it is, however, a much more refined problem than the older problem of proving under-valuation. Nevertheless, your committee believes that with such a mechanism in our law, much would be done toward encouraging our chemical industries.

#### TO CREATE A COAL TAR CHEMICAL INDUSTRY

8—According to the best information that your committee can gather, such an anti-dumping clause alone would not be sufficient, however, to create complete and independent domestic coal-tar explosives, dyestuffs and medicinals industries. It has been conclusively demonstrated during the past thirty years that the present tariff rate of 30 per cent on dyestuffs is not sufficient to induce the domestic dyestuff industry to expand at a rate comparable with the consumption of dyestuffs in this country and that, therefore, all dyestuffs made from coal-tar, whether they be aniline dyes or alizarin, or alizarin dyes, or anthracene dyes or indigo, so long as they are made in whole or in part from products of or obtainable from coal-tar, should all be assessed alike, namely, 30 per cent *ad valorem* plus  $7\frac{1}{2}$  cents per pound specific, and that all manufactured products of or obtainable from coal-tar, themselves not dyes or colors and not medicinal, should be taxed 15 per cent *ad valorem* and  $3\frac{3}{4}$  cents per pound specific.

#### TARIFF TO AID DYE INDUSTRY

9—The best information and judgment your committee can obtain is that the above manufactured products of coal-tar, not dyes and not colors and not medicinal, should carry one-half the duty of the finished coal-tar dye, and that the above rate of 30 per cent *ad valorem* and  $7\frac{1}{2}$  cents specific would probably be sufficient to encourage and enable domestic manufacturers to expand their operations to such an extent as to supply a very material increase in, if not the whole, of these commodities consumed in this country. The reason for a specific duty is to protect the domestic manufacturer in the manufacture of the relatively cheap dyes such as the cheap scarlets, the cheap yellows and the like, whose prices abroad are in the neighborhood of from 12 to 20 cents per pound; with dyes of that type 30 per cent *ad valorem* would not offer so serious an obstacle to importation and underselling thereof as does the  $7\frac{1}{2}$  cents per pound specific;

on the other hand, on dyes whose prices are \$1.00 and upwards per pound the function of the  $7\frac{1}{2}$  cents specific more nearly approaches zero; that is, with the cheap dyes the chief function lies in the specific portion of the duty and with the expensive dyes the chief function lies with the *ad valorem* portion of the duty.

This is said to be the price the nation will have to pay to have a complete self-contained and independent coal tar chemical industry. However, it must be remembered that if such an industry be created and importation of coal-tar products inclusive of intermediates and dyes is restricted, its ultimate effect upon the Federal revenues will have to be considered. *It will, therefore, be necessary to determine carefully if the advantages to be gained are equal to the price to be paid.*

#### PATENT LAWS

10—This committee is a unit in the belief that an alteration of our patent laws aiming at compulsory working or compulsory licensing would not be of any substantial benefit to this industry or to the country as a whole. Twenty-nine countries have attempted compulsory licensing clauses and fifty-six countries have attempted compulsory working clauses, and the best information your committee can obtain is that in none of these attempts has there been any appreciable measure of success. While it may be true that under extraordinary conditions, such as now exist, compulsory licensing might have some advantage, yet it is equally true that in normal times the disadvantage due to compulsory working or compulsory working would more than overbalance any advantage at all likely to be obtained under stress of unusual conditions.

11—In none of the countries where there have been working or licensing clauses or both, co-extensive with the existence of the coal-tar chemical industry, has there been established any real coal-tar chemical industry and your committee does not feel that an alteration in our present patent laws could be made which would be effective against foreigners and at the same time not be onerous and a hardship to domestic inventors. Your committee believes that in the long run and in the final outcome, our present system with regard to working and licensing is as efficient as that of any other country. In the dyestuff industry, in particular, there are so many non-patented commercial products and so many commercial products once patented, now free from patent restraint, that their production alone would form a basis for a very considerable industry, and your committee feels that the way to encourage that industry, if the establishment of that industry in this country be a national necessity, is through a change in the tariff and the additional anti-dumping feature in the administration of the tariff and not through any change in the patent laws. *Once established, such an industry could develop and ultimately cope with any foreign combination upon fair and equal terms.* Over 90 per cent of the tonnage and of the individual dyes used in the United States will be free from any patent-restraint within the next four years—over 75 per cent of the dyes are now in that condition.

#### AVAILABILITY OF RAW MATERIALS

12—The best information your committee has so far been able to gather is that this country can produce so-called coal-tar raw material in amounts sufficient for the needs of a complete domestic coal-tar chemical industry inclusive of explosives and dyes, provided there is a certainty of outlet as to volume and continuity. Those engaged in manufacture here do not want to expand unless the dye-users are willing to make corresponding contracts. In other words, it is a closed circle. If the dye-users will contract sufficiently with the dye-makers, the dye-makers will contract with the coal-tar distillers and the industry will take a start. The initiative rests wholly with the users; if they

cannot afford to contract, the dye-maker and the distillers cannot afford to make their contracts and additional investments.

#### COAL-TAR PRODUCTS

13—BENZOL, TOLUOL AND THE LIKE are produced in sufficient amount in present installations of by-product coke-ovens to provide all of these things that would be needed for a coal-tar chemical industry of a magnitude sufficient to supply the United States market; the separation of these materials from the gas that carries them is dependent upon the market and the demand therefor. There is no inherent defect in our coke-industry with regard to the actual making of these things; the only question involved is whether it be more profitable to burn the benzol, toluol and the like contained in the gas as a fuel than to separate them from the gas and from each other for purposes of sale. Ample supply can be provided before any plant that could use benzol and the like for dyestuff making could be erected in the United States, and thereafter the supply of these materials can readily be kept up to any requirement.

14—The materials of the preceding paragraph are the ones used in the coal-tar explosives industry as well as in the coal-tar medicinal and dyestuffs industries. Each of these three industries cooperates with the others to make full use of those materials; alone, none can fully make use thereof nor succeed; the correct and proper utilization of these materials requires successful co-existence of ALL THREE industries in one and the same country.

15—NAPHTHALENE AND ANTHRACENE are contained in the tars produced in the United States in an amount sufficient for the needs of a domestic dyestuff industry and it is merely a question whether it is more profitable to leave them in the creosote oil, where they now occur, or to separate them out of such oil and refine them for purposes of dye manufacture. Ample supply of either of them could be produced and provided at the same time or shortly after any plant could be erected in the United States for the use of these things in the production of dyes.

16—What has been said with regard to the supplies of naphthalene is also true of the supplies of CREOSOL.

17—All the CREOSOTE OIL contained in the total amount of coke-oven tar now made is separated from it and used. Increased production of creosote oil requires a greater production of tar, and a greater production of tar is dependent upon increased installation of recovery coke ovens.

18—PHENOL or CARBOLIC ACID supply is primarily dependent upon our deliberately selected method of coal treatment; to change that treatment so as to get more phenol would entail abandonment of other advantages which would not be compensated for by the increased amount of phenol so produced. Under present circumstances freights and haulages play an important part. At isolated plants, separated by considerable distances from each other, small amounts of phenol are produced and the separation of the phenol at such individual places would be economically unprofitable, and in order to concentrate this amount of phenol to or at a point where separation could be conducted profitably would entail freight haulages much in excess of the value of the phenol that would thus be transported.

19—The only source of phenol in sight is that produced synthetically from benzol by means of sulfonation and subsequent melting with caustic soda. This depends, in turn, upon our benzol supply and would be profitable only so long as the United States market is not killed by the dumping of foreign phenol thereon, whether such phenol be synthetic or distilled.

20—SALICYLIC production depends upon availability of phenol and the production of BENZOIC ACID depends upon the availability of toluol which has heretofore been discussed.

21—PHTHALIC ACID made from naphthalene by means of bichromate cannot successfully compete with that made by the mercury and sulfuric acid process which is protected by patents having about three years more to run.

#### MISCELLANEOUS CHEMICALS AND RAW MATERIALS

22—ACETIC ANHYDRIDE can be made without trouble in this country, and will be made in this country so soon as the domestic demand is large enough and steady enough to warrant the installation of a suitable plant.

23—NITRIC ACID: All countries, with the exception of possibly Norway and the countries importing from Norway, are dependent upon Chili for the raw material for making nitric acid. It will not be profitable to make nitric acid from air in the United States until the value of the electric horse power reaches a level of \$3 or \$4 a year, as it is in Norway.

24—AMMONIA and its salts all depend upon recovery coke ovens, and such recovery plants are increasing as fast as circumstances will permit.

25—BARIUM CHLORIDE and other compounds of barium may be made from domestic barytes. A number of attempts have hitherto been made, but with indifferent success. Factories established within the last year promise to be successful.

26—MAGNESIUM CHLORIDE of a sufficient purity to be used in the production of flooring is almost generally made from magnesite found in Greece, which is the only deposit known having sufficiently high purity; there are reports of suitable deposits in California and in lower California so that, with the completion of the Panama Canal, the question of freights, which seems hitherto to have stood in the way of developing these deposits, may be eliminated. Other sources, less remote from centers of consumption, and using other materials, *e. g.*, brine-waste, are about to be successfully operated.

27—MANGANESE in the form of pyrolusite is not known to occur in paying deposits in the United States; these are practically all in the Caucasus.

28—POTASH: In view of the great exertions that have been made for a number of years, both on the part of the federal government through a number of its departments and a great many different groups of capitalists, there is nothing to be said in this report that would be of any value with regard to increased production of potash either as fertilizer or as a chemical.

29—YELLOW PRUSSIAN AND SODIUM CYANIDE can be and have been made from domestic materials in such an amount as to provide practically the entire consumption, or a great portion thereof, in this country so long as there was a sufficient duty on them; the present duty is not enough to protect the American manufacturer, and those who were engaged therein have in large measure withdrawn from the business, but some are reported to be taking up manufacture cautiously and in limited amounts.

30—HYDROSULFITES in solution can be made from domestic materials without interference with any patent rights; the production of solid salts and derivatives are, however, still protected by patents that have a few years more to run.

31—SODIUM NITRITE is produced more cheaply as a by-product in Norway than it can be produced anywhere in the world; unless the price of the electric horse power in this country sinks to a \$3 or \$4 level per year, as in Norway, this product cannot be manufactured in the United States.

32—OXALIC ACID is and has been made to some extent in this country and the information coming to your committee is that suitable efforts are being made to expand the capacity of existing plants.

33—TARTARIC ACID AND CITRIC ACID: To make this country independent of others, with respect to tartaric acid and citric

acid, would call for radical changes on the part of our grape growers and our lemon growers as to the policy of their business.

It is probably true that edible grapes do not produce argols (the crude material for tartaric acid) very largely, and that our domestic lemons do not produce as large yields of juice (the crude material for citric acid) nor as high an acidity as do the Italian lemons; therefore, an independent supply of the raw materials produced in the United States for tartaric and citric acids is in the first instance an agricultural problem, and in the second instance a market problem.

#### GENERAL REMARKS

34—Finally, it should be pointed out that the United States is by no means the only country whose chemical and allied business has been strained or upset by the European war. Each and every other country has felt the strain. British committees have gone into this same subject of expanding British chemical industries and, not only that, but also into the question of making their very basic necessities, and the reports have so far been adverse to any immediate relief by domestic manufacture. The Boston Chamber of Commerce, through its committees, has arrived at the same conclusions for this country.

35—It is further clear that the stability of a complete domestic chemical industry, in so far as it depends upon foreign supplies, is bound up to a successful merchant marine and to an efficient foreign banking condition just as is all our foreign business.

#### FINDINGS

36—Your committee finds as follows, as to the facts:

I—Prior to the hostilities, domestic chemical industry was utilizing and exploiting every reasonable opportunity to its full extent.

II—Since the outbreak of hostilities, domestic industry has increased its output just as fast as physical means could be provided and physical obstacles overcome.

III—Since the outbreak of hostilities, domestic plants that had theretofore been shut down or partly dismantled because of disastrous foreign competition are said to have resumed operation, with caution.

IV—That a 30 per cent duty on some coal-tar dyes for over 30 years has not produced a real coal-tar dye industry in this country.

#### CONCLUSIONS

37—Your committee submits its conclusions as follows:

A—To prevent the unfair underselling alleged to be practised by foreigners in this country, the adoption of an effective anti-dumping clause.

B—The so-called coal-tar "intermediates" which are the basis of the coal-tar chemical industry, inclusive of explosives, medicinal and dyestuffs, should be assessed one-half of whatever the finished dyes are taxed for tariff purposes; *all* coal-tar dyes *without exception* should be taxed alike, namely, 30 per cent *ad valorem* and 7½ cents per pound specific.

C—Changes in the patent laws, such as by compulsory licensing or compulsory working clauses, are *wholly ineffective, do more harm than good and should not be attempted.*

Your committee recommends that this report be submitted to the appropriate committees of Congress. Further, that this report be forwarded to interested organizations.

BERNHARD C. HESSE, *Chairman*

J. B. F. HERRESHOFF	H. A. METZ
I. F. STONE	D. W. JAYNE
J. MERRITT MATTHEWS	ALLEN ROGERS

NEW YORK, November 6, 1914



## ORIGINAL PAPERS

### THE CEMENTING VALUE OF BITUMINOUS BINDERS

By LESTER KIRSCHBAUM

Received August 6, 1914

During the past ten years there has been a great development in the methods of valuating paving bitumens. Early attempts at determining these values were directed towards chemical determinations of properties or constituents which were thought to have an influence upon the quality of materials of this kind. Later developments have indicated that, with few exceptions, the valuable properties of paving materials are included more directly in their physical characteristics. The present status of the determination of paving values includes physical tests as the more important ones, leaving a few chemical tests directed towards determining the permanency of these products, and the care with which they have been prepared.

It will be generally agreed that a most important, if not primary physical property, which paving bitumens must possess is that of cementitiousness. For a long time efforts have been directed towards devising a means of measuring cementitiousness of bituminous binders, but so far nothing has been offered in this direction which has met with general approval. Among the tests commonly employed, that of ductility has been assumed to measure, or to be, in a general way, an indication of cementitiousness. While possibly there is some relationship between ductility and the cementing value of a given type of bitumen, it will be admitted that no mathematically direct relationship, if any, exists at all. So far, then, as our present means of determining cementing values are concerned, this most important feature must be arrived at by indirect interpretation of data which afford no exact means of determining such values.

The writer has for the past four or five years directed his attention to the development of a method for directly and mathematically expressing the cementing value of plastic binders. Various means have been employed in the effort to determine this factor, but all have been discarded as it developed that they fell short of measuring the properties sought for. The writer has, at various times, devised bending or shearing tests; has investigated the tensile strength of briquettes of binders and mixture of same with mineral particles; has investigated the strength of briquettes joined together by films of binder, and has experimented with methods of determining adhesiveness and cohesiveness. These various attempts, while in some cases giving valuable information, have failed, either through the inability to devise a means of obtaining concordant results, or for the reason that the properties actually measured in these efforts did not directly represent the cementing value property sought for. For example, in making tests of briquettes of non-bituminous material stuck together with a film of binder, it is not only difficult, if not impossible, to obtain concordant results on account of variations in

thickness of film, etc., but results obtained do not measure binding value, but measure cohesiveness. When tests of this kind are made, the briquettes fracture with a cleavage, leaving a film or part of a film on either end of the briquette. The property so recorded is *cohesiveness* or the ability of the material to stick to itself. Any method which measures strain endured by the film of asphalt in detaching itself without cleavage or fracture from a foreign surface measures *adhesiveness*. In either case, the operation fails to determine the cementing value or the ability of the material to bind particles together under the conditions of service.

If we analyze the results obtained upon a number of materials through a series of tests for tensile strength (meaning in this case the maximum strain endured in fracturing a briquette of bitumen) we shall find that two different materials may sustain the same maximum stress and indicate the same cohesiveness, but that one material will sustain this strain for but a short time before fracture, while another material will not only sustain the same maximum strain, but will endure it during a longer period or through a much longer distance of elongation. For example, a given type of asphalt cement at a certain penetration will, during application of strain, withstand a maximum of say, three units before fracturing. Another asphalt of certain penetration will withstand the same strain. In the former case, however, after this maximum is reached, an appreciable strain can be sustained for many times the elongation that may be sustained with the latter material. Cohesiveness results in such cases would indicate equality, but as a practical consideration, the latter material might be entirely unfit for paving purposes, and even from superficial observation might not indicate nearly the cementing qualities of the former. Such results, then, not only become misleading and contrary to practical observations, but fail entirely to give us an indication of the property sought for.

The adhesiveness of bituminous binders may be determined by means of a suitable apparatus. While the adhesiveness is a matter of importance in the effectiveness of bituminous application to cold road metal by pouring processes, nevertheless, in considering hot mechanical mixtures, the adhesiveness appears to play little part in holding together the mineral aggregate. When asphalt pavement cracks or fractures or displaces, an examination of the points of fracture discloses that the films of bitumen coating the particles have fractured or cleaved, and not that the bitumen has pulled off the mineral particles through lack of adhesiveness. In other words, the adhesiveness is always greater than the cohesiveness and the binding value. No mechanically measured results of adhesiveness need therefore be considered as a factor in this discussion, although the adhesiveness is a factor in considering pavements built by penetration methods.

What, then, represents the cementing value of a material of this kind? Cementing value must mean the ability of the bitumen to bind or hold together against rupture, particles of mineral matter which it coats or covers. Upon analyzing the conditions applying, it becomes evident that to break apart the bond between any two mineral particles held together by a coating of plastic bitumen, a certain tension must be applied for a certain time or space of action. The application of a tension over a certain distance infers the necessity for the film of binder to elongate at the point of contact of the two particles. The actual amount of elongation may be extremely small, but the relative amount in proportion to the thickness of the coating may be very great. That elongation does necessarily take place must be admitted from practical experience, which has taught us that a certain degree of plasticity or softness of our binders is essential to prevent cracking of pavements. The effect of advancing the softness of the binders is to favor their ability to yield and elongate under strains. Cracking is therefore minimized by superior ability of a soft binder to elongate over a hard binder of the same kind. If this ability to elongate were not essential, and if it actually did not take place in the binder between the particles of aggregate, it is apparent that the hardest binders would be the best, as they would be capable of sustaining greater strains than the softer binders. It will be seen therefore that the ability to elongate is an essential feature, and must operate, otherwise our conclusions would lead us in the direction contrary to actual experience.

Referring again to our consideration of two particles of aggregate bound together, it is necessary, in order to produce fracture or to disrupt the bond, to apply a certain tension over a necessary distance. The product of these factors is work done. The binding value of a plastic binder is then limited to the amount of tension it can sustain over a given distance, or is directly proportionate to the work done in producing fracture or failure of a given unit of material.

An apparatus was accordingly devised for the purpose of recording the factors above mentioned, namely, strain applied over distance. The apparatus in its final form is shown in Figs. 1 and 2. It consists of a rectangular box insulated and lined with galvanized iron or copper. An inclined plane or runway is attached to the box, the lower end of which reaches the bottom of the box, and the other end projects an equal distance outside. This runway carries a carriage through which passes a screw actuated by a set of gears adjustable to the desired speed. Upon the carriage is maintained a dynamometer, to the end of which is connected a flat brass rod, which extends along the runway to within a few centimeters of the end, and of the bottom of the box. This rod is graduated in metric units, and passes under an adjustable bridge at which the readings are recorded during travel of the rod. The runway is edged with guides of sufficient width for the free passage of the briquettes. The arrangement and position of the carriage makes it possible to apply a tension through the rod in a straight line

to briquettes at the lower end of the runway with the box filled with water. At the lower end of the runway is permanently fastened a small boss or projection to which one end of the briquette is attached, the other

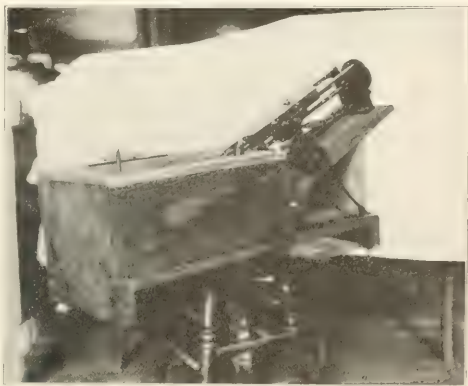


FIG. 1

end being attached to the rod connected with the dynamometer. The position of the bridge gives readings of elongation of the briquette, regardless of the movement of the carriage and dynamometer. The form of briquette adopted is that commonly known as the "Dow" moulds which are used for making ductility tests. These moulds have a minimum cross section of 1 sq. cm.

In working out the method of manipulation, it was of course necessary to determine a constant temperature at which the test should be made. The temperature selected was 5° C. or 41° F. This was selected for several reasons. In the first place it was

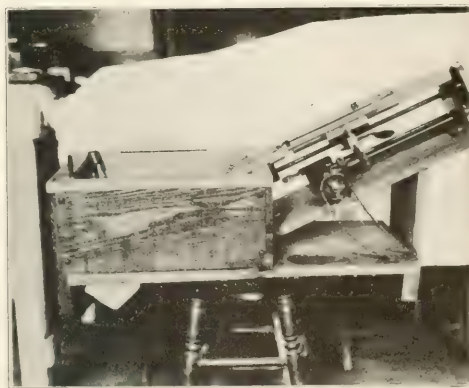


FIG. 2

necessary to obtain sufficiently large readings upon the dynamometer. At normal temperatures, bituminous materials of this kind are ordinarily capable of withstanding but very little strain. Secondly, the

strains which produce fracture and cracking in a pavement in actual service are greatest during cold weather. Again, a low temperature being necessary, the temperature of  $5^{\circ}\text{C.}$ , was selected as being easy to maintain constantly with ice and water.

On account of the plastic nature of the material operated upon, and its tendency to elongate under strain, it was necessary to determine upon a uniform means of application of load. It was evidently impossible to set a uniformly increasing load for the reason that, as the material elongated, and its cross section became smaller, it would be necessary to rapidly accelerate the rate of elongation or travel of the dynamometer towards the end of the operation, in order to increase the strain. This would become impracticable as a matter of manipulation, and would be subject to large variation through personal equation and through inability to take the required readings sufficiently rapidly. It was found necessary after many trials to adopt a *uniform rate of travel of carriage and dynamometer*. This is in accord with practical conditions, inasmuch as any strain set up in a pavement would be induced at a variable rate of application,

that in applying strain to the briquette by means of a dynamometer traveling at a uniform speed, the briquette has at first slight tendency to elongate under application of strain, until a maximum is reached, when the rate of elongation of the briquette exceeds the rate of travel of the carriage and dynamometer, at which point the dynamometer begins to register values below the maximum attained, until finally the briquette is either fractured at a reduced cross section through elongation of the material, or the dynamometer returns to zero without fracture of the briquette. An essential difference from the method of determining ductility is that during the entire period of elongation, the material is under substantial strain. Ductility or elongation values that include the distance traveled by an extremely fine thread or filament of bitumen are misleading and immaterial.

In making the test, as finally adopted, the briquettes are prepared in the usual manner as for ductility test, and are placed in the test box at  $5^{\circ}\text{C.}$  They are held for about three-quarters of an hour at this temperature before making the test. When ready, one end of

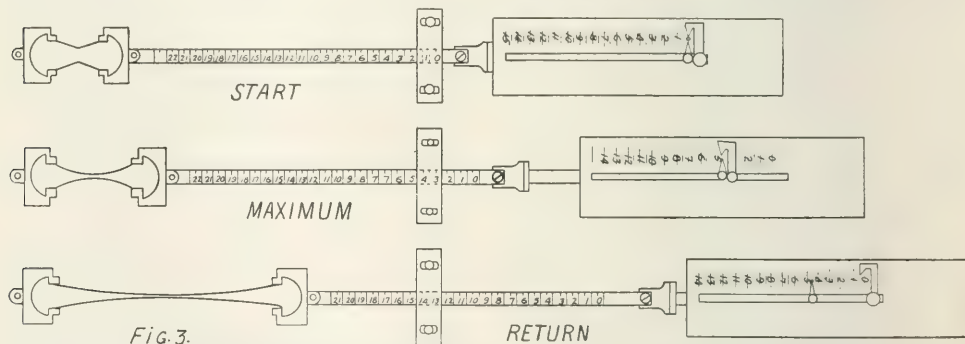


Fig. 3.

depending on the ability of various binders to yield or elongate without fracture. It is apparent that under the same conditions of volume change in a pavement a soft binder would yield and conform more easily to the necessary change, thereby allowing much less strain to be set up than with a hard binder.

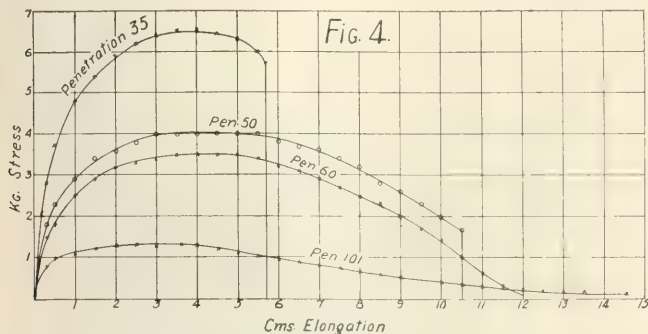
Various trials were made at different speeds in order to determine what speed was most adapted to securing concordant results, and distinguishing to the greatest degree the differences between various materials. Speeds between 1 to 10 cm. per minute were tried upon the same materials. It was found that the higher speeds had a tendency to effect too sudden application of strain, and, with the harder materials, to produce fracture in the corner of the briquettes rather than at the point of minimum cross section. Again, at the faster speeds, it became difficult to take the readings near the time of fracture owing to the rapid travel of the rod and the pointer of the dynamometer. After various trials it was found that a speed of travel of the carriage and dynamometer at the rate of 1 cm. per minute provided to the greatest extent for the factors indicated above. It will be understood

the briquette is hitched to the fixed post at the bottom of the box on the runway, and the dynamometer brought into position so that the end of the rod attached to same may be fastened to the other end of the briquette. The apparatus is driven mechanically, and the carriage is started by closing the split-nut which brings it into contact with the screw. When the end of the dynamometer begins to move over its zero mark, the bridge over the rod is adjusted to the zero mark on the rod. Carriage and dynamometer continue to travel at the rate of 1 cm. per minute, and readings of the dynamometer are taken at every half centimeter of elongation as shown by the rod. This is continued until the briquette fractures or elongates through its maximum back to zero strain. The dynamometer carries a maximum pointer and is graduated in tenths of a kilogram, and the zero mark is taken as one-tenth kilogram, which includes the weight of the briquette and the frictional resistance of parts. The position of the rod and boss are such as to lift the briquette slightly off the runway when the strain is applied, so that no friction results on this account during the application of strain. Fig. 3 illustrates



the position of the briquette and dynamometer at various stages of test.

The results of the data obtained in these determinations may be graphically recorded. The distances elongated are recorded as abscissae, and the strain as ordinates. Fig. 4 gives a typical example of results obtained upon the same material of different consistencies under this method of test. The areas en-



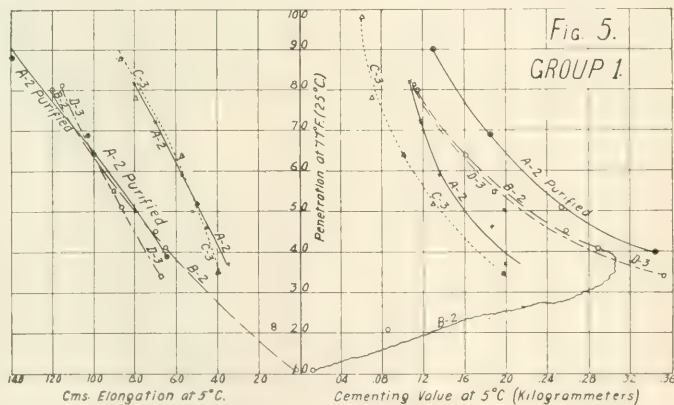
closed by these curves represent the product of the strain applied and the distance of its application, or the work done. The unit of value is expressed as kilogram-meters. This area may be obtained from the graphical plot of the result, or may be secured much more quickly, and sufficiently accurately, by addition of the ordinates. The readings are taken for every 0.5 cm. or 0.005 of a meter. Every unit of ordinate therefore represents 0.005 kilogram meters, and the sum of the ordinates multiplied by this factor gives the area or the work done in kilogram meters. Expressed mathematically, the formula for calculating the result is  $\Sigma Y \times 0.005$ . This is sufficiently accurate for practical purposes. Referring again to Fig. 4, it will be noted that the same material at different consistencies requires widely varying amounts of work for failure. With the harder materials, a comparatively sharp curve is obtained, which reaches a certain maximum, and then becomes less as the material elongates faster than the carriage travels. When the cross section is reduced to a point at which it is unable to withstand the strain induced, it breaks. With the materials of the softer consistency there is a tendency of the curve to flatten out and to become larger as the material is more plastic. A consistency is finally reached at which the material is able to progress through to its maximum and back to zero (or 0.1 kg.) without fracture. All tests were obtained in duplicate, and the results indicate a limit of accuracy of 0.02 kg. meter from an average, on the highest results, to a much closer agreement upon the lower values. Exception to this accuracy

is noted upon the hard brittle materials, which are unable to elongate uniformly without setting up internal strain, due to the corners of the briquettes.

Having established a satisfactory method of determining the value sought for, it was desired to outline a series of investigations covering the following points:

- 1—Survey of the characteristics of commercial products with special reference to determining the degree of differentiation possible with the various materials.
- 2—The possibility of valuating fluxes by this method.
- 3—Test of the commercial products, the chemical characteristics of which indicate inferior preparation.
- 4—The determination of a possible effect upon cementing value induced by improper preparation upon a series of products made known under known conditions.
- 5—The determination of standards of value necessary for practical application.

In order to take complete information of the characteristics of commercial products, it is necessary to collect such data as would represent a wide range of consistency for each material. The refined asphalt was accordingly used and fluxed with the kind of flux ordinarily used in practice. Determinations were made upon each material at a number of different consistencies, and these cementing values were graphically expressed as abscissae and the consistencies as ordinates. The various materials examined were grouped into three classes according

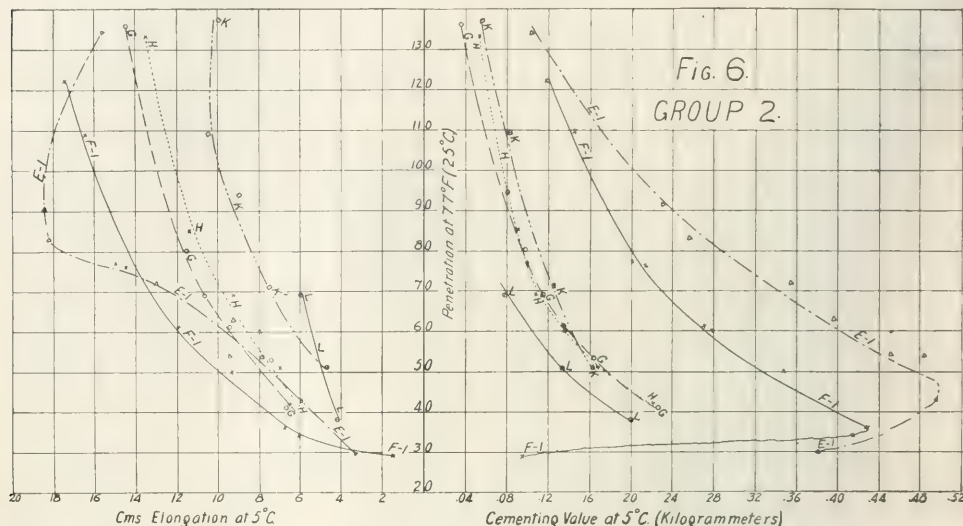


to their origin. Record was made of the cementing value as determined by the data presented before, together with the elongation and the maximum strain sustained. These data are given in Table I (page 981).

Group 1 contains asphalt cements prepared from solid natural bitumens, and Groups 2 and 3 include products made from natural liquid bitumens.

Results obtained are given graphically in Figs. 5, 6 and 7. It was found desirable to plot elongation in order to complete the means of interpretation of the results. The graphical presentation of this data

pull. Such procedure, however, would minimize the differences between these materials at those consistencies at which such differences are of greatest importance.



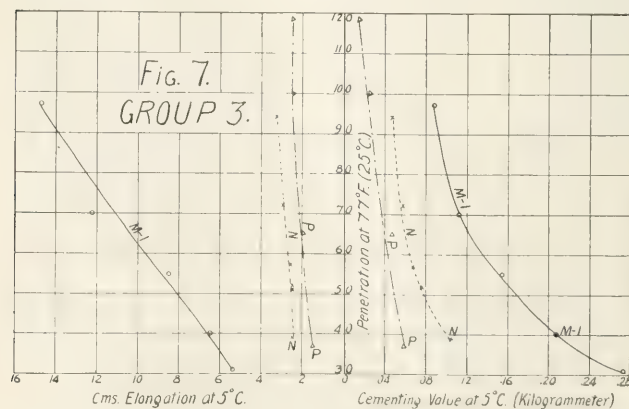
indicates a relationship between consistency and cementing value on one hand, and consistency and elongation on the other. By referring to plates, it is possible to compare the values of any of the materials at the same penetration. It will be noted that the cementing value increases generally as the consistency becomes harder, but when a certain hardness is reached, there appears to be a breaking off in the values determined in this way, owing to the brittleness and the inability of the material to yield without internal

The effect of the presence of mineral matter upon the binding value and elongation is illustrated in case of material A-2, which was examined with the mineral matter in, and with the mineral matter removed. The presence of mineral matter in these materials lowers the result obtained for cementing value, although the cohesiveness or maximum strain recorded is greater for the same consistency with the mineral matter in. The apparent lowering of cementing value is due to the lesser elongation produced under strain, and

to the fact that the bitumen when examined with its contained mineral matter is actually softer than indicated by penetration of the whole.

The increase of binding value with hardness, and the increase of elongation with softness is quite in accord with practical observations. For example, if a material be laid under light traffic at, say, 65 penetration, experience has shown us that we must reduce the penetration under heavy traffic, in order that the mineral particles may be bound together more solidly to resist impact and displacement. On the other hand, when we lay a pavement at 65 penetration for light traffic, we require greater ability in the material to elongate in order

to resist cracking, than we do under heavy traffic. This is true because, as is well known, heavy traffic tends to knead the pavement and relieve the stresses set up by changes of temperature. It will be



strains induced by the form of briquettes. This is a factor dependent upon the speed of the pull, and in all likelihood there would be a continuation of the curves beyond the present points at a slower rate of

TABLE I—GROUP 1 FIG. 5  
Asphalt "C" and Flux 3

Pen. at 77° F.	Max-imum strain	Average	Cementing Values	Average	Elongation Cms.	Average
35	5.2-5.7	5.7	0.199-0.198	0.199	4.0-4.0	4.0
52	3.2-3.0	3.1	0.134-0.126	0.130	5.0-5.0	5.0
64	2.3-2.2	2.25	0.101-0.101	0.101	5.5-6.0	5.75
78	1.4-1.1	1.35	0.077-0.063	0.070	7.5-8.5	8.0
98	1.1-1.0	1.05	0.060-0.063	0.062	8.5-9.0	8.75

## Asphalt "B" and Flux 2

41	5.1-5.0	5.05	0.269-0.308	0.288	6.0-7.0	6.5
51	3.8-3.6	3.7	0.278-0.233	0.255	9.5-8.0	8.75
59	2.6-2.4	2.5	0.154-0.158	0.161	9.0-11.0	10.0
80	1.6-1.5	1.55	0.114-0.103	0.111	12.0-12.0	12.0
45	4.3-4.3	4.33	0.259-0.257	0.258	7.0-7.2	7.1
11	6.4-7.2	6.8	.....	0.017	0.2-0.25	0.22
22	7.3-...	7.3	0.087-.....	0.087	1.2-1.2	1.2

## Asphalt "A" and Flux 2

37	6.3-6.5	6.4	0.194-0.202	0.198	3.5-3.5	3.5
50	4.2-4.4	4.3	0.215-0.186	0.201	6.0-6.0	5.75
59	2.3-2.9	2.85	0.119-0.152	0.136	5.0-7.5	5.25
72	2.3-2.3	2.3	0.111-0.125	0.118	6.5-7.5	7.0
82	2.0-2.1	2.05	0.107-0.109	0.108	8.5-7.5	8.0
46	4.3-4.5	4.5	0.197-0.172	0.185	4.8-4.3	4.6

## Asphalt "A-2" Purified

39	6.0-6.1	6.05	0.338-0.348	0.343	6.5-6.5	6.5
69	2.4-2.4	2.4	0.183-0.164	0.174	10.0-10.5	10.25
88	1.6-1.6	1.6	0.137-0.123	0.130	13.0-15.0	14.0

## Asphalt "D" and Flux 3

34	5.8-6.6	6.15	0.324-0.379	0.352	6.5-7.0	6.75
55	2.7-2.6	2.65	0.191-0.185	0.188	9.0-9.0	9.0
81	1.3-1.5	1.4	0.105-0.121	0.113	11.5-12.0	11.75

## GROUP 2—FIG. 6

## Asphalt "E" and Flux 1

30	13.7-13.6	13.65	0.369-0.393	0.382	3.2-3.4	3.3
43	9.9-9.6	9.75	0.469-0.503	0.486	5.5-6.4	5.95
54	6.6-6.5	6.5	0.470-0.430	0.450	8.0-7.7	7.85
72	4.0-4.3	4.15	0.343-0.364	0.353	15.0-11.0	13.0
63	5.0-4.8	4.9	0.401-0.389	0.395	9.0-9.5	9.25
91	2.75-2.85	2.62	0.224-0.234	0.229	18.0-19.0	18.5
83	2.9-2.8	2.85	0.251-0.263	0.257	18.0-18.5	18.25
134	1.2-1.3	1.25	0.099-0.103	0.101	16.0-15.5	15.75

## Asphalt "F" and Flux 1

29	5.9-7.2	6.8	0.074-0.149	0.097	0.9-1.7	1.5
34	7.3-7.7	7.4	0.415-0.382-0.441	0.413	6.5-5.7-6.1	6.1
56	7.5-6.9	7.2	0.463-0.394	0.428	7.0-6.5	6.75
50	5.1-...	5.1	0.354-0.344	0.347	8.0-10.5	9.25
61	2.8-...	2.8	0.269-...	0.269	12.0-...	12.0
76	2.8-...	2.8	0.212-...	0.212	13.0-...	13.0
77	2.5-2.4	2.45	0.206-0.195	0.201	14.5-15.5	15.0
109	1.6-1.6	1.6	0.133-0.155	0.144	16.0-17.0	16.5
122	1.1-1.4	1.25	0.111-0.123	0.117	17.0-18.0	17.5

## Asphalt "H" and Flux "H"

42	3.9-4.0	3.95	0.216-0.225	0.220	6.5-6.5	6.5
51	2.6-3.3	2.93	0.169-0.163	0.166	6.5-7.5	7.0
60	3.3-2.35	2.33	0.138-0.15	0.137	8.0-8.0	8.0
69	1.7-1.8	1.75	0.102-0.114	0.108	9.0-9.5	9.25
77	1.8-1.8	1.7	0.103-0.095	0.099	9.5-9.5	9.5
85	1.2-1.2	1.2	0.0938-0.0878	0.091	11.5-11.5	11.5
133	0.5-0.5	0.5	0.0517-0.0518	0.051	13.5-14.0	13.75

## Asphalt "G" and Flux "G"

41	3.8-4.1	3.95	0.221-0.229	0.225	7.0-6.5	6.75
53	2.8-2.9	2.85	0.165-0.158	0.162	7.5-7.2	7.35
61	2.2-2.1	2.15	0.137-0.134	0.136	9.5-9.5	9.5
69	1.8-1.7	1.75	0.124-0.105	0.115	10.5-11.0	10.75
80	1.4-1.5	1.45	0.093-0.103	0.098	11.0-12.0	11.5
136	0.3-0.3	0.3	0.036-0.033	0.035	14.0-14.5	14.25

## Asphalt "L"

38	5.5-...	5.5	0.199-...	0.199	4.2-...	4.2
51	3.4-3.1	3.25	0.146-0.122	0.134	4.5-5.0	4.75
69	2.0-...	2.0	0.077-...	0.077	6.0-...	6.0

## Asphalt "K"

51	3.8-4.0	3.9	0.150-0.173	0.162	4.5-5.0	4.75
71	4.4-2.4	2.4	0.129-0.121	0.125	7.5-7.5	7.5
94	1.5-1.6	1.55	0.077-0.082	0.080	9.0-9.0	9.0
109	1.3-1.2	1.25	0.085-0.082	0.084	10.5-10.5	10.5
137	1.0-0.9	0.95	0.059-0.054	0.057	9.5-10.5	10.0

## GROUP 3—FIG. 7

## Asphalt "M" and Flux 1

31	5.5-6.0	5.75	0.263-0.284	0.273	5.5-5.3	5.4
40	3.8-3.9	3.85	0.213-0.202	0.208	6.2-6.8	6.5
55	2.6-2.2	2.4	0.167-0.141	0.154	8.5-8.5	8.5
70	1.3-1.4	1.35	0.112-0.113	0.112	12.5-13.0	12.25
97	0.9-0.9	0.9	0.088-0.086	0.087	14.5-15.0	14.75

## Asphalt "N" and Flux "N"

39	4.7-4.6	4.65	0.105-0.103	0.104	2.5-2.5	2.5
52	3.3-3.4	3.35	0.075-0.077	0.076	2.5-2.5	2.5
57	2.8-2.8	2.8	0.068-0.062	0.065	2.5-2.5	2.65
72	2.2-2.3	2.25	0.058-0.060	0.059	3.0-3.0	3.0
94	1.8-1.7	1.75	0.045-0.049	0.047	3.0-3.5	3.25

## Asphalt "P" and Flux "P"

37	4.3-4.3	4.3	0.059-0.059	0.059	1.5-1.5	1.5
100	1.2-1.2	1.2	0.025-0.023	0.023	2.4-2.5	2.5
118	0.9-1.0	0.9	0.015-0.016	0.016	2.5-2.5	2.5
65	2.5-2.7	2.6	0.045-0.050	0.047	2.0-2.0	2.0

noted that the cementing value is not directly proportionate to the elongation, and that in some cases the binding value of two different materials at the same penetration is very similar, whereas their ability to elongate at the same penetration is appreciably different. Likewise, particularly at the lower penetrations, some materials elongate to practically the same extent, yet their cementing values are widely different. It is evident from the study of this graphical data, that it is not only necessary to consider the elongation as a factor in the cementing value, but it is also necessary to consider it apart from the cementing value. If this were not so, our pavements would be less liable to crack when laid at the harder consistencies. It appears, therefore, that while the cementing value indicates the ability of the material to bind aggregate together, a minimum ability to elongate is also necessary to avoid cracking. This is well illustrated with material "N" which, when laid, has sufficient cementing value to bind the mineral particles together for light traffic, but which has a very pronounced tendency to crack. Its binding ability at no consistency would be sufficient for conditions of heavy traffic. It will further be noticed that the general tendency of the elongation curves is to straighten upward beyond a certain consistency, and in some cases, even to retreat. This indicates that beyond a certain amount, fluxing not only results in less binding value, but results in reduced ability to elongate, and that nothing would be gained, so far as plasticity is concerned, by further fluxing. In the case of materials "P" and "N," there would hardly be any consistency at which the material might be handled which would overcome the tendency to crack. This in a practical way has been actually found to be the case. Attention may be called, at this point, to the fact that various materials showing the same maximum strain or cohesiveness possess widely different cementing values. For example, asphalt "G" at 53 penetration shows 2.85 kg. maximum strain. The same value for cohesiveness is shown by asphalt "E" at 83 penetration, yet the cementing value of this latter greatly exceeds that of asphalt "G." This is a typical example which indicates the ability of this test to differentiate beyond any ordinary tension tests.

Table II is given showing the results of investigations made in the effort to determine the possibility of valuating various fluxes. In this series of tests the same asphalt was used throughout, and was fluxed with different fluxes, the cementing values and other data being determined as indicated before. These are given in Table II.

Graphical results are shown in Fig. 8. It will be noted that the cementing values of these materials are progressively greater as the fluxes tend towards asphaltic base, with this exception that the paraffine combination shows slightly better values than the light-semi-asphaltic. This is due to the fact that much less paraffine base flux was used to produce the consistencies noted than in the case of the light semi-asphaltic flux. When, however, the elongation



curves are examined, a progressive increase without exception is noted in ability to elongate as the fluxes used partake more of an asphaltic character. It will

TABLE II—FLUX TESTS FIG. 8  
R. A. and Paraffine Flux

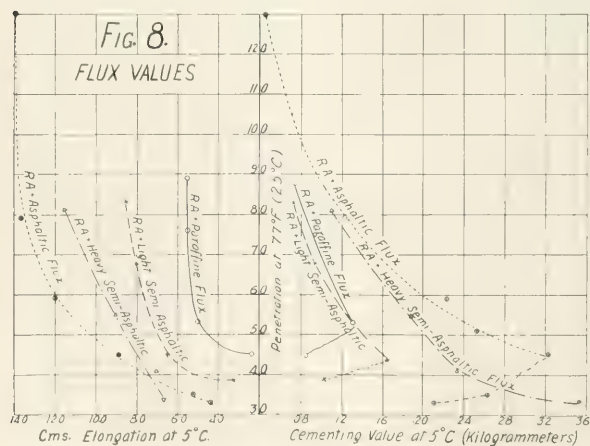
Pen at 77° F.	Maximum strain	Average	Cementing Value	Average	Elongation Cms.	Average
45	3.9-4.0	3.95	0.082-0.083	0.083	2.5-2.3	2.4
53	3.0-3.1	3.05	0.115-0.144	0.130	4.6-5.0	5.0
88	1.7-1.7	1.7	0.072-0.075	0.074	5.5-5.5	5.5
76	2.1-2.1	2.1	0.093-0.095	0.094	5.5-5.5	5.5
R. A. and Light Semi-Asphaltic Flux						
39	3.8-3.9	3.85	0.092-0.114	0.103	3.0-3.7	3.35
68	1.5-1.5	1.5	0.096-0.096	0.096	8.2-8.0	8.1
83	1.2-1.1	1.15	0.077-0.067	0.072	8.5-8.5	8.5
44	3.0-3.0	3.0	0.188-0.141	0.165	7.4-5.5	6.45
R. A. and Heavy Semi-Asphaltic Flux						
34	5.8-6.5	6.15	0.325-0.379	0.352	6.5-7.0	6.75
55	2.7-2.6	2.65	0.191-0.185	0.188	9.0-9.0	9.0
81	1.3-1.5	1.4	0.105-0.121	0.113	11.5-12.0	11.75
R. A. and Asphaltic Flux						
140	0.4-...	0.4	0.043-...	0.043	14.0-...	14.0
79	1.4-1.3	1.35	0.119-0.125	0.122	13.0-14.5	13.75
59	2.7-2.6	2.65	0.246-0.198	0.222	13.0-11.0	12.0
45	4.1-4.2	4.15	0.316-0.327	0.322	9.0-8.8	8.9
35	6.0-5.8	5.9	0.282-0.246	0.264	5.0-5.5	5.25
31	3.6-3.6	3.6	0.254-0.249	0.252	8.5-8.5	8.5
33				0.210		4.4

be noted that the ability to elongate would become even a more sensitive indication of the character of the flux itself than the cementing value. The practical necessity for considering this ability to elongate is aptly illustrated here. This refined asphalt used with paraffine fluxes has proven unsatisfactory in practice. Under light traffic, pavements laid with this have shown sufficient binding qualities to hold the mineral particles together, but the tendency to crack is very decided. On the other hand, this refined

materials have been encountered which gave indication, from analysis, of having been poorly prepared—so much as to warrant their rejection for use. A few of these samples were on file, and were available for cementing value tests. These materials were generally refined asphalts of from 30 to 40 penetration, reduced from liquid albumen. They were subjected to the cementing value test at the consistency at which they were obtained, and then fluxed with the same asphaltic flux to a consistency corresponding to paving penetration, in order to afford comparison with normal products of the same type. The determination of cementing value and elongation are given in Table III, together with the principal analytical characteristics.

These results are graphically shown in Fig. 9, and are given in connection with a curve showing the quality of an average acceptable commercial sample of material prepared from similar crude. It is evident from the study of these results that the chemical indications of inferior preparation shown by the high fixed carbon and per cent insoluble in carbon tetrachloride are confirmed by actual lowering of the cementing qualities, and elongation values.

In order to confirm the indications of lowering of cementing qualities with accompanying evidences of poor preparation, products were made in the laboratory from the same asphaltic base crude oil under known conditions. These were made in a small still,



asphalt with light semi-asphaltic flux has shown, in a practical way, that the cracking tendency is greatly reduced in laying at a sufficiently high penetration, and it has been much more satisfactory than the previous combination, even though its cementing value is not greater. The material with the asphaltic flux and the heavy semi-asphaltic flux have been eminently successful under service conditions. It is evident from the above that the method described furnishes a means of determining the value of various fluxes and their suitability in asphalt combinations.

During the course of commercial practice, various

and were prepared at temperatures of 525°, 700° and 825° to 850° F. at the end of the distillation. Four runs were made, two of which were conducted at the last named temperature. In the first three runs, the materials were not pushed to a hard penetration, but of the last two runs at 850° F., one was pushed to a very hard consistency. In order to obtain an indication as to the comparative extent of cracking which took place, composite samples of the distillate were tested for gravity. In the first two runs, samples were taken from the still at various points of consistency indicated hereafter. In the fourth run, the material, as stated, was pushed to a very hard penetration and fluxed back with well prepared asphaltic base flux from the same crude. All of these samples were tested for cementing value, and those samples most nearly corresponding in consistency or penetration were examined for their main chemical characteristics. These results are given in Table IV (page 984) and are shown graphically on Fig. 10. On account of the insufficient number of points of elongation secured, no attempt was made to draw a smooth curve covering these points. Inspection of the above tabulated results shows that very little change or decomposition has occurred under 700° F. in running down to the consistencies noted. The material prepared at 850° F. gives evidences of substantial decomposition. This is indicated by a lighter

gravity of distillate and falling off in solubility in carbon disulfide. The gravity of distillate in runs T-3 and T-4 hard are, of course, not strictly comparable owing to the different consistencies to which these were pushed. As a consequence of the decomposition that has occurred, there follows a substantial increase of fixed carbon *over normal*, and the conversion of part of the bitumen to a form insoluble in carbon tetrachloride. The differences between products obtained in the two T-4 runs show that not only is temperature a factor in decomposition, but also the degree to which the operation is pushed, or the degree of "concentration" resulting. This latter

to note the persistency with which material prepared from this crude retains its cementing value even when badly decomposed; and although showing evidences in this direction which would cause its rejection under standard specifications, its cementing value has not been reduced below an acceptable minimum. As to whether or not materials so prepared, and possessing the characteristics of the last named product would *retain* the cementing value indicated, is a matter requiring investigation before any conclusion can be drawn as to the effect of the features noted. It will be seen, in referring to commercial products prepared from crude of this character, that the loss of cementing

TABLE III—FIG. 9

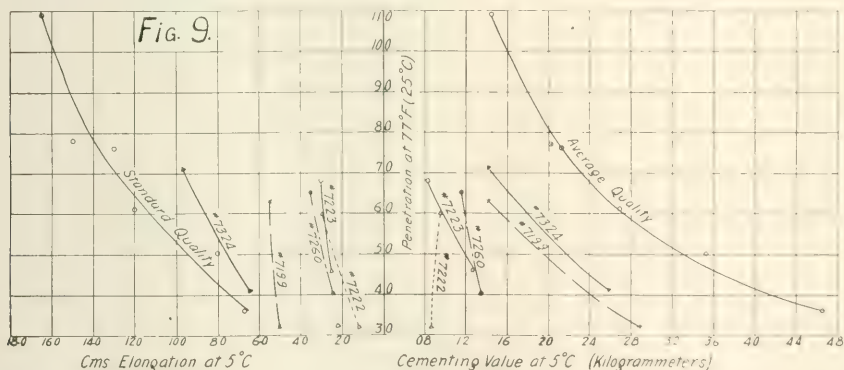
No.	7199	fluxd	7222	fluxd	7223	fluxd	7260	fluxd	7324	fluxd
Pent. at 77° F.	32	64	32	60	46	68	40	65	41	71
Duct. at 77° F.	60 cm.		4.5 cm.		7.5 cm.		7.0 cm.		1.2 per cent	
5 hr. loss.	0.4 %		0.6 %		0.8 %				65 cm.	
Per cent hardening.	25.0		25.0		36.9				43.9	
CS <sub>2</sub> soluble.	99.7		98.9		99.0		99.0 %		99.7	
Mineral.	0.2		0.2		0.2				0.2	
Difference.	0.1		0.9		0.8				0.1	
CCL <sub>4</sub> soluble.	97.0		90.0		94.4		95.9		97.9	
Fixed carbon.	16.6		18.6		17.7				16.9	
Cementing value at 5° C.	0.289		0.085	0.096	0.126	0.082	0.136	0.117	0.258	0.141
Elongation at 5° C.	5.0	0.141	1.2	2.9	2.5	3.0	2.5	3.75	6.5	9.75

is in confirmation of the investigations made by the writer some time ago.<sup>1</sup>

It will be observed from the inspection of the graphical data that the most cementitious materials were produced at the lower temperatures, and that the cementing values decrease as the conditions of preparation become more severe. While the differences in cementing value between materials produced at 525° and 700° F. are slight, there is a substantial difference between these results and those obtained with the materials produced at 850° F., and between these latter, prepared at substantially the same temperature, but pushed to a varying degree of hardness.

value is much greater with slighter evidences of decomposition than is obtained from the products prepared in the laboratory. No explanation of these variations is offered, aside from the indications given by these commercial products of having been prepared by other methods, than those involving straight distillation.

It is evident that this method of determining cementing values is capable of distinguishing between products prepared with more or less care, and that a reduction in cementing properties follows as a consequence of decomposition occurring during preparation.



There is marked loss in cementing value in the material pushed to hard penetration and fluxed back, and the evidences of decomposition are very decided. In fluxing this hard material (T-4) back with well prepared flux, approximately equal quantities of flux were required to bring it back to 62 penetration. The effect of the introduction of so large a quantity of well prepared flux has, of course, minimized the loss of cementing value. Nevertheless, it is astonishing

In the previous discussion, various commercial asphalts which have been used in paving work have been examined, together with their appropriate and inappropriate fluxes. There has also been observed the effect on asphalt derived from liquid bitumen, of improper conditions of preparation. It remains, therefore, to analyze the data obtained, in connection with practical results, and to determine, if possible, what cementing characteristics appear to be necessary for the successful binder. Discussion of this

<sup>1</sup> Municipal Engineering, 35, 349

phase of the matter will be confined to only one form of construction, namely, sheet asphalt pavements.

From long experience with various materials observed in this discussion, and in segregating those binders which, in the writer's observations, have been successful and unsuccessful, certain tentative values may be set which should differentiate the successful or acceptable cement from the non-acceptable. Carefully considering this matter in connection with practical results, the lowest cementing value which is considered acceptable under conditions of light traffic is

materials laid under traffic, calling for a penetration of 35 to 40, with materials of the first group, the writer would prescribe for such traffic a minimum cementing value for the bitumen used of about 0.24 kilogrammeters, and elongation limits between four and six centimeters. Maximum limits of elongation are set as well as minimum limits for the reason that above the maximum limits of elongation, is the accompanying higher consistency, which results in too soft a cement under conditions of hot weather. These limits are, of course, suggestive, and will be modified according

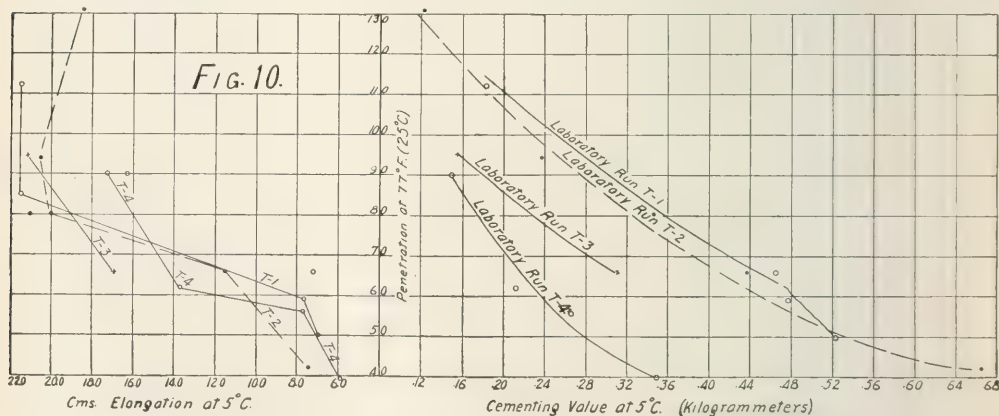
TABLE IV—FIG. 10

	T-1	T-2	T-3	T-4 hard	T-4 fluxed
Temperature still	522° F.	700° F.	850° F.	850° F.	...
Gravity of distillate at 60° F.	21.2	21.2	26.2	25.6	...
Pushed to penetration	50	42	66	2	...
Fluxed to penetration at 77° F.	59	66	...	...	62
Ductility at 77° F.	115 + cm.	115 + cm.	102 cm.	...	37.0 cm.
Fixed carbon	5.5 per cent	7.0 per cent	13.1 per cent	26.4 per cent	15.2 per cent
Soluble in CS <sub>2</sub>	99.6	99.7	98.9	85.3	93.3
Soluble in CCl <sub>4</sub>	99.6	99.7	97.5	67.9	87.1
Cementing value at 5° C.	0.478	0.439	0.311	...	0.212
Elongation at 5° C.	7.7 cm.	11.5 cm.	17.0 cm.	...	13.75
Melting point	...	...	...	217° F.	...

set at 0.08 kilogrammeters. This value, if taken alone, will include some materials which, although able under light traffic to bind the mineral particles in a sheet asphalt pavement together, are prone to develop cracking. As stated previously, it is necessary not only to consider the cementing value alone, but also to consider the ability of the binder to elongate, in order to prescribe those which have the property of holding together mineral aggregate without undue tendency to cracking. For light traffic, this elongation value is set between the limits of 8 cm. and 14

to the individual experience and ideas of those who might employ these tests. It is probable that an empirical formula may be devised giving the relationship between traffic units and cementing-elongation values in such a way as to indicate the necessary characteristics applicable for any intensity of traffic.

There remains another factor which may influence the valuating of materials in accordance with these characteristics, and that is, the possible rate of loss of cementing value which will be shown upon tests carried out over a prolonged period of time. As is well



cm. for the pure bitumen. Below these values are found, in the writer's experience, unsuccessful materials for the class of construction referred to, and corresponding to these values are found those which have demonstrated satisfactory use under light traffic.

As previously indicated, pavements under heavy traffic require stronger and more cementitious binders with less need of these binders to elongate. It is difficult to describe accurately conditions which would be understood by all to be designated as heavy traffic. Keeping in mind, however, service records of ma-

known, various bituminous materials harden with age and suffer marked loss of ductility upon standing, sometimes for comparatively short periods of time. It is likely that the materials here examined would likewise show variable rate of loss of cementing value and elongation with age, particularly those materials showing the effects of severe treatment in preparation. Data of this kind covering a period of time or indicating the same effect of accelerated tests will be of considerable importance in fully determining the relative values of various types of binders.



It is the intention of the writer to take up these phases of the subject, but owing to the time necessary to compile complete data, it is considered advisable to present the foregoing in the expectation that the methods employed may be improved upon by others interested, and that the features indicated may be simultaneously investigated by independent observers.

It is suggested that this test not only covers all of the data heretofore furnished by the ductility test, but in addition furnishes direct information as to the cementing values of the materials examined. The elongation values determined during the cementing value tests afford a more accurate and truly representative indication of ductility than the test usually employed. The elongation values determined by this method have an advantage of being taken at a temperature at which such properties come into play most effectively in pavements, and are recorded only while the binder is capable of withstanding an appreciable strain. These values are not clouded by the fine hair-like filaments into which bitumen is drawn at normal temperatures, and which have no significance in determining any valuable property. In addition, it is difficult, if not impossible, by the usual method, to differentiate between materials having a ductility in excess of certain limits fixed by the devices usually employed, which cannot be extended much beyond 100 centimeters with any significant results.

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### HYSTERESIS TESTS FOR RUBBER

By EARLB L. DAVIES

Received September 25, 1914

The expert usually judges a piece of rubber by means of a crude hysteresis test which he performs by stretching a small strip with his fingers. Experience enables him to judge closely, but by no means accurately, small differences between two samples; it does not enable him to standardize his tests, nor to make his results available to others. Several machines have been devised to perform and record these tests graphically, but they have not come into their full usefulness, due to the difficulty encountered in translating the graph into terms which are intelligible and comparable. The object of this paper is to point out and explain some of the relationships between the mathematical equation for the curve and the properties of the rubber being tested, and to point out the close relationships which some of the tests, made in this laboratory, show between the theoretical curve and actual curves made by the machine.

The accompanying figure shows the typical form of curve produced by the machine. The ordinates represent tension and the abscissae, stretch. Cheneveau and Heim<sup>1</sup> have shown that this curve has the equation:

$$x = cy + a \sin^2 by \quad (1)$$

and that when OB is drawn tan. to the curve OD at O,

$$c = \tan. / YO B.$$

From (1)

$$a \sin^2 by_1 = x_1 - cy_1$$

Since

$$c = \frac{m_1}{y_1} \text{ and } z_1 = x_1 - m_1$$

then

$$z_1 = x_1 - cy_1$$

or

$$z_1 = a \sin^2 by_1 \quad (2)$$

In like manner it may be shown that  $z_2 = a \sin^2 2by_1$  (3)

From (2)

$$\sin^2 by_1 = \frac{z_1}{a}$$

Since

$$2 \sin^2 A = 1 - \cos 2A$$

then

$$\frac{2z_1}{a} = 1 - \cos 2by_1$$

or

$$\cos 2by_1 = \frac{a - 2z_1}{a} \quad (4)$$

From (3)

$$\sin^2 2by_1 = \frac{z_2}{a} \quad (5)$$

Since

$$\cos 2A = 1 - \sin^2 A$$

then

$$\cos^2 2by_1 = 1 - \sin^2 2by_1$$

and from (4) and (5)  $\left(\frac{a - 2z_1}{a}\right)^2 = 1 - \frac{z_2}{a}$

Whence

$$a = \frac{4z_1^2}{4z_1 - 2z_2} \quad (6)$$

Since

$$\cos^2 A = 1 - \sin^2 A$$

From (2)

$$\cos^2 by_1 = 1 - \frac{z_1}{a} \quad (7)$$

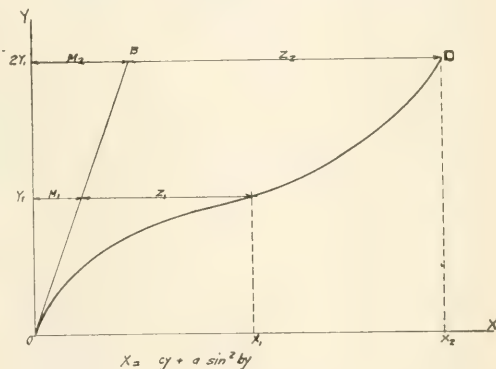
From (6) and (7)

$$\cos^2 by_1 = \frac{z_2}{4z_1} \quad (8)$$

Whence

$$by_1 = \cos^{-1} \sqrt{\frac{z_2}{4z_1}} \quad (9)$$

That these terms are not so mysterious as they appear, becomes evident after an analysis of the above proof. Thus we find the constant "c" is dependent solely upon the initial resistance of the rubber to stretching; it will be largest for a pure gum stock and



become relatively smaller and smaller as the stock is more heavily compounded. From the relationship in Equation 6 we can readily see that in the case of a pure gum stock where the stretch is long and uniform, ( $m_1$ ) and ( $m_2$ ) having been large "a" will be relatively large, in comparison with a "tread" stock which will be strong and cause the entire curve to be fairly steep, but will be small in comparison with a "whiting stock," which is characterized by an initial stiffness after which it offers comparatively little resistance to stretching. Equation 9 shows that for pure gum or tread stocks  $\cos b$  will be small and "b" consequently large.

The ease with which these values could be standard-

<sup>1</sup> "Sur l'extensibilité du caoutchouc vulcanisé," *Compt. rend.*, p. 320, Feb. 6, 1911; also, "The Rubber Industry," (1911).

ized in specifications for a given stock is apparent, and the value of such standards both from the point of the manufacturer and the buyer is obvious.

We have done some work in this laboratory to find how closely the curve computed from the equation agrees with the actual curve, of which the following example is typical: For our work we used the "Schwartz Rubber Testing Machine." Test specimens were cut from a "Goodyear" auto inner tube, and from curves drawn in testing these specimens we obtained constants which gave the equation:

$$x = 1.17y + 2.06 \sin^2 34.6y$$

Another tube made by the same formula was selected at random and a curve drawn from a sample of this tube. Assuming various values for  $y$ , the  $x$  to correspond was computed from the equation and compared with the same values as measured on the curve. The results were as follows:

$y$ Inches	$b$	$y$	$x$ (computed) Inches	$x$ (from curve) Inches	Diff. Inches
0.2	6	55	0.26	0.26	0.00
0.5	17	18	0.77	0.78	-0.01
1.0	34	36	1.84	1.86	-0.02
1.5	51	54	3.04	3.05	-0.01
2.0	69	12	4.14	4.08	+0.06
2.5	86	30	4.78	4.70	+0.08
3.0	76	12	5.26	5.17	+0.09
3.5	58	48	5.61	5.60	+0.01
4.0	41	36	5.71		

These are actual measurements from the curve representing only arbitrary values for  $x$  and  $y$ .

#### CHEMICAL LABORATORY

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### A STUDY OF THE EFFICIENCY OF VARIOUS METHODS FOR THE FILTRATION OF SUGAR SOLUTIONS<sup>1</sup>

By ALFRED E. ROBERTS

Received May 13, 1914

#### INTRODUCTION

Owing to the difficulty of filtering sugar solutions of high density and the limited number of standard methods in practice, this investigation was undertaken to compare several filtering media as to speed of filtration, brightness of filtrate and the duration of efficiency.

All sugar houses are using modes of filtering which are more or less satisfactory but perfection has never been achieved, and their laboratories have always faced the unsolved problem of filtering the house liquors of high density and locating irregularities quickly.

The purpose of this work has been primarily to perfect a rapid filtration process for sugar laboratories and secondarily to improve house practice.

There is scarcely any literature on the subject, though some reference to different filtering media to be used on a large scale can be found.<sup>2</sup>

#### EXPERIMENTAL

The materials used in this research were the three different grades of cloth commonly employed in sugar refineries which will be designated in this paper as

<sup>1</sup> A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science to the Faculty of the Graduate School of New York University.

<sup>2</sup> Noel Doerr, "Cane Sugar," p. 281.

thin bag, thick bag, close bag; alundum, white filter paper No. 597 Schleicher and Schull, Eimer and Amend's Best gray filter paper, 40-mesh sand, asbestos, Fuller's earth, infusorial earth and sawdust.

Suction and different hydrostatic pressures were considered and many modifications of apparatus were tried. The majority of the experiments, however, were conducted with a cylindrical tube 1½ inches in diameter, having a barrel 6 in. in length and a stem of 3 in. This special tube is represented in Fig. 1.

In nearly every case the tube was used in an upright position and at all times it was surrounded with a jacket of hair felt in order to maintain a comparatively constant temperature. That the temperature did not drop very low during short filtrations may be seen by referring to Fig. 2. In general, the solutions of sugar were about 30° Bé density, and before filtering the temperature was raised to 180 F. The cold apparatus caused the solutions to drop about 20° during the first 10 min. but after that time the temperature decreased very slowly. A more elaborate and efficient device could have been arranged, but complicated apparatus is undesirable for rapid work in a sugar laboratory.

During the preliminary experiments with the bag filters, it was found that greater speed of filtration could be procured by using a circular piece of wire gauze instead of a perforated porcelain plate to support the cloth; hence the apparatus adopted for the first series of filtrations was the cylindrical tube mentioned above with the wire gauze support in the bottom; resting on this was a cloth cut to fit the tube and this was held in position by a tight-fitting rubber gasket.

Each bag filter was tested as to rate of filtration of an undefecated solution, clearness being disregarded, and the typical results are herein recorded in Fig. 3. As would be expected from the weave and general

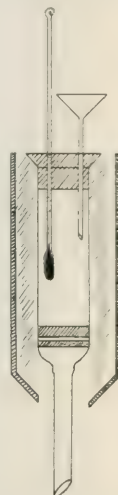


FIG. 1.—SPECIAL TUBE FOR FILTRATION OF SUGAR SOLUTIONS OF HIGH DENSITY

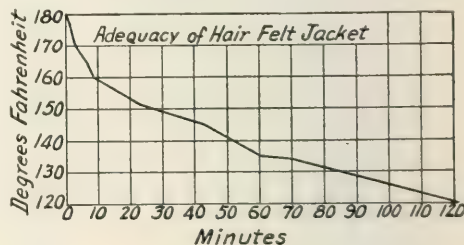


FIG. 2

texture of the cloth, the thin bag gave the highest rate of filtration, the thick bag second and the close bag third; the fact that the thin bag allowed 100 cc. to pass through in 7 min. suggested its adoption, while the

thick cloth permitted only about one-fifth and the close cloth one-tenth that amount to pass through in the same time.

These conditions were then modified in one respect. A thin bag filter attached to a wire was placed on the

the filters was to allow them to stand overnight and note the numbers of cc. which had passed through during that time. The numbers were simplified so that the least efficient filter is represented by unity.

A great deal of difficulty was experienced in determining the exact time of filtrates becoming clear. The only satisfactory device used was made by attaching to the stem of the filter tube a straight calcium chloride tube, the end of which was bent in such a way that the bulb was kept constantly full of liquor (see Fig. 6). By holding a magnifier over this bulb its contents could be examined for clearness. Time was counted from the instant solutions were poured upon the respective filters and the results were as follows:

	Min.		Min.
Thin bag, one thickness.....	17	Gray paper.....	6
Thin bag, two thicknesses (a).....	4	Asbestos.....	2
Thick bag.....	7	Sand.....	2
Close bag.....	4	Sawdust.....	3
Alundum.....	2	Fuller's earth.....	Never
White paper.....	3	Infusorial earth.....	Never

(a) Filtration was very slow, only 15 cc. passing through in 26 min.

fixed thin bag and as soon as the filtration became slow the upper cloth was removed. This modification hastened the process in a marked degree (Fig. 4) with the thin and thick cloth, but the action of the close bag was not sufficiently rapid to make it a competitor.

Tests with each of the filtering media proved that perfect clearness could not be obtained without defecation; hence, all solutions in subsequent experiments were defecated either with Horne's dry subacetate of lead or with bone-black paste neutralized with lime.

In determining the relative values of cloth, alundum, sand, asbestos, Fuller's earth, infusorial earth and sawdust, numerous filtrations were found necessary in order to perfect manipulation. The regular tube was used and the solutions were kept at a constant head of six inches while ascertaining the rates of filtration, the amounts possible to pass through the respective filters,

In filtering with alundum a special disc was made to fit the standard tube and the same rubber gasket as

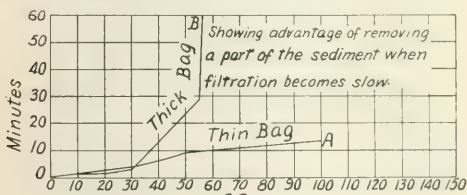


FIG. 4

and the clearness of filtration. Fuller's earth and infusorial earth could not be arranged in this form of apparatus to produce satisfactory results.

It is evident from the following table and Fig. 5 that the material used for defecation influences both the rate and duration of filtration. The time of 30 min. was chosen arbitrarily for the sake of uniformity in making comparisons.

RELATIVE RATES OF FILTRATION AND LIVES OF FILTERS			
BONE-BLACK DEFECATION		LEAD SUBACETATE DEFECATION	
FILTER	Cc. in 30 min. life	FILTER	Cc. in 30 min. life
Sawdust.....	150	Thin bag.....	32.5
Asbestos.....	35	Asbestos.....	23
Thin bag.....	23	Thick bag.....	23
Sand.....	22.5	Close bag.....	20
Close bag.....	16	Sand.....	19
Thick bag.....	14	White paper.....	10.5
White paper.....	13	Alundum.....	10.5
Gray paper.....	11	Gray paper.....	9.5
Alundum.....	8		

As the solutions ceased to filter after prolonged intervals the mode of determining the relative lives of

Sugar Solution 30.5° Be. Defecated with Bone-Black Paste and Subacetate of Lead

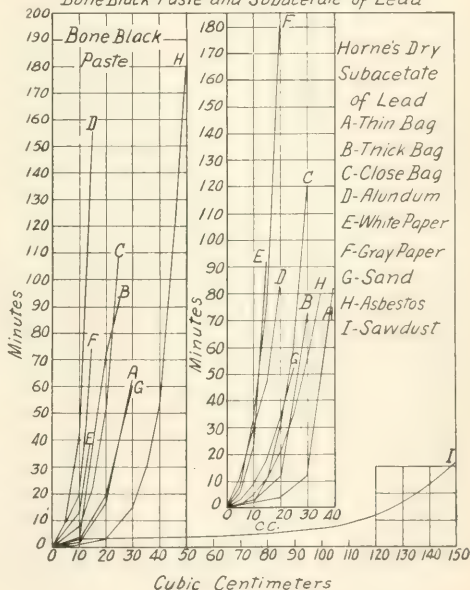


FIG. 5

was used with the cloth and paper filters was placed in close contact with it to prevent the solution from passing over the edge of the disc. The asbestos filter was prepared by first placing in the tube a porcelain filter plate; then a layer of washed asbestos of fine fiber was poured upon the plate to the thickness of one-eighth of an inch. The sand used was 40-mesh and the depth most satisfactory was 3 in. The sawdust filter was prepared by filling the tube loosely with the material and then packing tightly until the



depth was 4 in. The sawdust thus measured weighed 27 g. A small wad of glass wool was used in the stem of the tube to prevent sawdust from passing into the filtrate.

In order to hasten filtration, suction was employed with the different media, but in each case it was a failure because clearness was always destroyed by suction.



FIG. 6  
DEVICE FOR  
DETERMINING  
CLEARNESS OF  
FILTRATES

Favorable results, however, were obtained by increasing the height of the column of liquor. A marked increase in efficiency was demonstrated in the case of the thin bag by using 3 ft. hydrostatic pressure. Fig. 7 compares this medium with a head of six in. and 3 ft. and also in a Buchner funnel having a diam. of 5 in. It is evident at once that it is better to increase pressure than surface.

An attempt was made to hasten filtration through the thin bag by inverting the whole apparatus and operating it like the Danek filter. The object of this style of filtering is to prevent the solid matter from becoming too thickly deposited on the filtering medium and thus checking the passage of the liquid. One foot head was used in this experiment. There was no disappointment as to increasing the rate of filtration, but the arrangement proved a total sacrifice to clearness of the filtrate. As long as the apparatus was kept full of solution a constant stream of filtrate flowed showing conclusively that the thin bag, at least, is efficient for producing a bright filtrate only after its interstices become filled with solid matter.

Besides the aluminum disc made to fit the regular filter tube made for this investigation several experiments were conducted with the same medium but in form of a thimble 4 in. long and 1 1/4 in. in diam. In one arrangement the thimble was fitted with a one-hole stopper of rubber into which a tube was passed nearly to the bottom of the thimble. The other end of the tube extended into a graduated tube enclosed in a suction flask, while the thimble was immersed in a beaker of defecated sugar solution kept at 180° F. with a low flame underneath the beaker. Suction was applied 35 min. but only 25 cc. of the solution passed through the filter.

The most successful filtering with the thimble was accomplished by inverting it in a straight cylindrical tube fitted with a one-hole rubber stopper. The end of the thimble was tightly inserted in a groove cut in the stopper and a tube extended from the inside of the thimble through the stopper and into a suction flask. Hair felt was used as a jacket to prevent too great a decrease in temperature. With this arrangement the following results were obtained:

SOLUTION 31° BAUMÉ, DEFECCATED WITH LEAD 6 IN. HEAD					
Cc.	Min.	Cc.	Min.	Cc.	Min.
5	1	30	14	50	40
10	2	35	24	55	40
20	5	40	27	60	51
25	9	45	29	65	67

The filtrate was clear in 3 min. and, as nothing could be drawn through after 65 cc. were filtered, this amount represents the life of this size thimble under

these conditions. Owing to the fact that suction had been unsuccessful in previous experiments in producing a clear filtrate, the pump was not started until the solution began to come clear at the end of three min.

Sawdust, having surpassed all other media under consideration, was adopted as the standard material for carrying on a series of experiments in which it was hoped to arrange a device for determining whether or not a solution had been properly defecated. The plan was to adjust the apparatus in such a way that the filtrates would have their respective end-points of cloudiness at certain points for stated degrees of defecation.

The regular six-inch filter tube was used but in the top was fitted a one-hole rubber stopper carrying a funnel six inches in length, making a head of eight inches, and a tube was attached to the stem of the filter tube and bent upward to a level with the top surface of the sawdust which weighed 27 g. and was packed

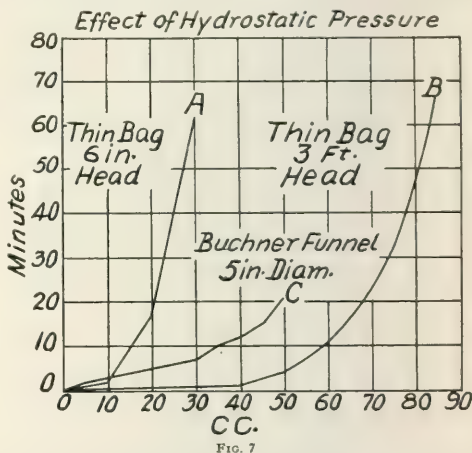


FIG. 7

down to a thickness of four inches. This attachment was used in order to saturate thoroughly the filtering medium and prevent channels before the drip commenced.

Perfectly defecated wash sugar liquor at 33° Baumé was poured into the apparatus and time was counted from the instant of the filtrate reaching the highest point in the outlet tube. A beautiful filtration ensued and would have been satisfactory for any purpose but the one in question. The filtrate being clear, from the first did not furnish a definite point of becoming clear, so the amount of sawdust was decreased one-half. Numerous filtrations were conducted on this basis and in each case the cloudiness disappeared after the first 15 cc. A 50 per cent defecated solution was prepared by mixing equal parts of a fully defecated wash sugar liquor at 32° Baumé and an undefecated wash sugar liquor at 34° Baumé. All filtrates with this solution became clear after 30 cc.

In filtering a 25 per cent defecated solution all filtrates with one exception became clear after 40 cc.; the irregular one cleared after 45 cc.

At this stage the apparatus was modified again. The filtering medium was cut down to six grams and the one-hole stopper was replaced by a two-hole stopper to provide for a tube provided with a pinchcock to be closed as soon as the air was expelled with solution. In order to increase the head and thus secure a more rapid rate of filtration the outlet tube was lowered as soon as the filtrate reached the highest point in the bend.

The first filtration under these conditions was with an undefecated solution. It was allowed to run over night and the filtrate never became clear, demonstrating the necessity of defecation.

Then a fully defecated solution was tried and the first 100 cc., requiring 15 min., was cloudy; after this, it ran clear. This result indicated that there was not a sufficient layer of sawdust, so the amount was increased to 10 g. and the outlet tube was left in place for the rate of filtration was too rapid with one foot head. With this arrangement a rapid and satisfactory filtration was secured, 40 cc. dropping in three minutes and after this the filtrate was clear. Several duplicates were run with the same results except for time,

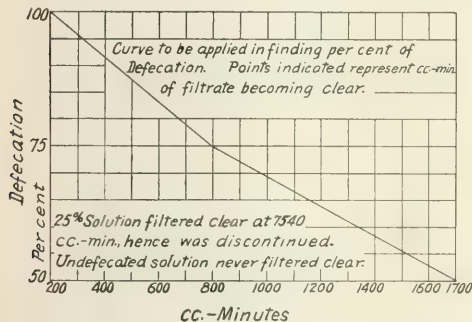


FIG. 8

which varied slightly but not much, as a Hofmann clamp attached to the outlet tube was adjusted to regulate the flow.

A 50 per cent defecated solution was filtered and the point of becoming clear varied from 60 to 100 cc. according to rate of filtration. A 75 per cent defecated solution behaved in the same way except that usually it became clear at about 60 cc. The 25 per cent defecated solution never filtered clear as long as observed. On careful consideration of both volume and time it was evident that clearness depended on a combination of the two, and hence in the concluding experiments the point of the filtrate becoming clear was expressed in "cc.-min." In all fully defecated solutions the filtrate ceased to be cloudy at about 200 cc.-min., the 75 per cent defecated at about 300 cc.-min., the 50 per cent defecated at about 1700 cc.-min., while the 25 per cent defecated solutions never produced a bright filtrate.

The liquors passing through the bag filters in the refinery required about 20 min. to become clear after defecation, while the same solutions became clear in the adopted laboratory filtering device in 3 min. This

relation of house to laboratory could be applied with advantage.

Fig. 8, plotted for this particular apparatus, indicates that the preconceived theory works out in practice, and thus the device can be applied in sugar laboratories to determine at once whether the house liquors are properly defecated.

The results of this investigation seem to prove that sugar refineries should adopt as the universal filtering medium sawdust or some closely allied material. This is confirmed by A. Aulard<sup>1</sup> in his paper on the "Use of Cellulose as a Filtering Substance in Sugar and Other Industries." Sawdust can be easily washed; it is very simple to use, needing no complicated presses, etc.; it is available and cheap; rapid filtration is assured and clear, bright liquors can be secured in a minimum time. The main problem would be in concentrating the increased volume of sweet water which would necessarily be produced in washing the sawdust.

#### SUMMARY

- 1—Defecation is necessary with all filtering media.
- 2—Sawdust or some form of wood waste is the most satisfactory for obtaining rapid and clear filtration both for refineries and laboratories.
- 3—To hasten rate of filtration it is better to increase hydrostatic pressure than resort to suction, increased surface of filtering medium, or to invert the filter to keep it free from a deposit of solid matter.

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#### THE ABSORPTION OF GASOLINE VAPOR IN NATURAL GAS BY FUMING SULFURIC ACID

By R. P. ANDERSON AND C. J. ENGELDER

Received September 25, 1914

Orndorff and Young<sup>2</sup> apparently were the first to discover that propane is attacked by fuming sulfuric acid. Worstall<sup>3</sup> has investigated the sulfonation of hexane, heptane, and octane by fuming sulfuric acid and found that the reaction takes place readily at the boiling point of the hydrocarbon that was being used, but that cold fuming sulfuric acid is without apparent action on the liquid hydrocarbon. He found<sup>4</sup> also that methane and ethane are slowly absorbed by fuming sulfuric acid, the absorption being more rapid in the case of ethane than in the case of methane.

During the analysis in this laboratory of a sample of natural gas which carried a small amount of gasoline vapor, there was obtained a small decrease in volume (0.1 to 0.2 cc.) during the usual treatment with fuming sulfuric acid. Aside from this indication of the presence of olefines the gas appeared to contain only members of the paraffin group and a small amount of nitrogen. Combustions were made on gas which had been treated with fuming sulfuric acid and on untreated gas. The results of the combustions were figured as methane and ethane, the predominating hydrocarbons, and the untreated gas appeared to

<sup>1</sup> See original communication in *Eighth International Congress of Appl. Chem.* (Appendix) **21**, 489-491.

<sup>2</sup> *Am. Chem. J.*, **15** (1893), 249.

<sup>3</sup> *Ibid.*, **20** (1898), 664.

<sup>4</sup> *J. Am. Chem. Soc.*, **21** (1899), 245.

contain more ethane and less methane than the treated gas. This could be explained by the assumption that the fuming sulfuric acid had absorbed some of the gasoline vapors, since the removal of a small amount of these vapors would lessen the apparent percentage of ethane as calculated from the results of a combustion. If this assumption is correct, longer treatment with the fuming sulfuric acid should result in a larger decrease in volume and a greater difference in the apparent amounts of methane and ethane before and after the treatment. Accordingly, a sample of gas was passed back and forth for fifteen minutes over fuming sulfuric acid that was contained in the customary pipette for this reagent. A decrease in volume of 2 cc. was obtained. The approximate results of the combustions that were made are shown below:

	Per cent CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	N <sub>2</sub>	Total
Before treatment with H <sub>2</sub> SO <sub>4</sub> .....	72	27	1	100
After treatment with H <sub>2</sub> SO <sub>4</sub> .....	75	21	2	98

The decrease of 2 cc. that was obtained after a more lengthy treatment with the reagent than is usually given indicates the absorption of gases or vapors other than those of the olefine group since the absorption under the customary conditions amounted to but 0.1 to 0.2 cc. The change in the relative amounts of methane and ethane as calculated from the results of the combustion indicates that the portion that was absorbed contained more gases or vapors of high molecular weight than the portion that remained. The average number of carbon atoms per molecule of hydrocarbon in the portion absorbed by the fuming sulfuric acid may be computed from the data at hand. For example:

Let  $m$  represent the number of molecules in 1 cc. of the gas, and  $x$  the average number of carbon atoms per molecule of hydrocarbon in the portion absorbed by the fuming sulfuric acid;

then  $72\ m + 2 \times 27\ m =$  the number of carbon atoms in 100 cc. of the original gas,

and  $75\ m + 2 \times 21\ m =$  the number of carbon atoms in the unabsorbed gas.

$72\ m + 2 \times 27\ m - 75\ m - 2 \times 21\ m = 9\ m =$  the number of carbon atoms in the absorbed gas,

and  $x = \frac{9\ m}{2\ m} = 4.5$ .

The average number of hydrogen atoms per molecule of hydrocarbon may be computed in similar fashion and thus it appears that the gases removed by the fuming sulfuric acid had an average composition of C<sub>4.5</sub>H<sub>11</sub> while the untreated gas averaged C<sub>1.26</sub>H<sub>4.52</sub>.

To determine whether this behavior of the paraffin hydrocarbons toward fuming sulfuric acid might be made the basis of a method for the examination of natural gas for the presence of the higher hydrocarbons, gasoline vapors<sup>1</sup> in particular, the following experiments were performed.

#### BEHAVIOR OF REAGENT WITH REPEATED USE

The absorbing power of the reagent should remain practically constant when treated successively with

<sup>1</sup> For a discussion of the methods in use at the present time, see Burrell and Seibert, *This Journal*, 5 (1913), 895; also Merriam and Birchby, *Ibid.*, 5 (1913), 824.

different portions of the same natural gas for the same time in order that reliable comparisons might easily be made between the amounts of gasoline vapors in different samples of natural gas. If the reagent should deteriorate rapidly on being used, comparable results could be obtained only with fresh reagent and the inconvenience and expense of its frequent renewal would be a serious drawback to its use.

The fuming sulfuric acid that was used in studying the behavior of the reagent with repeated use contained 30 per cent SO<sub>3</sub>, and was placed in an absorption pipette such as is used in the Dennis modification of the Orsat apparatus,<sup>1</sup> in order to effect as rapid an absorption as possible. The upper end of the reservoir chamber of the pipette was connected by means of a rubber stopper and glass tubing with a trap similar to the one used in the same modification of the Orsat apparatus to protect the reagents from the air. In this case, the trap was filled with sulfuric acid and the space between the reagent in the pipette and the sulfuric acid in the trap was filled with natural gas at the beginning of the experiments. This arrangement decreased considerably the interchange of gas and air through the reagent and proved very essential for lengthy contact between gas and reagent. A water-jacketed burette containing mercury was used in connection with this special pipette. The natural gas that was employed was drawn from a cylinder of the compressed gas obtained from the United Natural Gas Company, Oil City, Pennsylvania. The contact between each sample of gas and the reagent was limited to thirty passages which were made in a uniform manner, and readings of the remaining gas volume were taken at the end of each six passages. The sulfur dioxide was not removed before these readings. At the end of the thirty passages, the sulfur dioxide was removed by potassium hydroxide, and the oxygen by an alkaline solution of pyrogallol. Since the original gas contained practically no oxygen the decrease that was obtained on the last absorption served as a measure of the interchange of natural gas and air through the reagent in the pipette and the sulfuric acid in the trap during the absorption. Combustions were performed on two separate portions of each residue and the results were computed as methane, ethane and nitrogen. The results obtained are shown in Table I.

Number of sample	TABLE I					
	1	2	3	4	5	6-10
Volume after 6 passages.....	3.5	1.9	1.4	1.3	1.0	0.9
Volume after 12 passages.....	5.8	3.6	2.8	2.4	1.9	1.8
Volume after 18 passages.....	7.5	5.0	3.8	3.5	2.9	2.7
Volume after 24 passages.....	9.1	6.3	4.8	4.5	3.7	3.6
Volume after 30 passages.....	10.5	7.1	5.7	5.7	4.6	4.5
Volume after KOH.....	10.8	7.5	6.1	6.2	5.5	5.5
Volume after Pyro.....	12.0	8.1	7.5	6.8	6.1	5.8
Per cent CH <sub>4</sub> .....	72.7	79.1	76.4	79.3	76.7	78.1
Per cent C <sub>2</sub> H <sub>6</sub> .....	11.8	11.8	12.3	12.4	15.3	14.7
Per cent N <sub>2</sub> .....	3.5	1.0	3.8	1.5	1.9	1.4
Carbon atoms per molecule in portion absorbed.....	2.70	3.04	4.01	3.45	3.31	3.30

The first five columns of figures in the above table contain the readings that were made during the absorptions on the first five samples, as the numbers at the top indicate. In general, the amount absorbed at the end of each six passages and after the removal of SO<sub>2</sub> decreased with each successive sample

<sup>1</sup> See Dennis, "Gas Analysis," p. 86.



up to the fifth. From the fifth sample to the tenth the reagent gave approximately uniform results and the average of the various corresponding readings from runs six to ten inclusive is given in the last column. The lack of uniformity in the readings that were obtained from the first four samples may, no doubt, be largely accounted for by the solubility in the reagent of the various constituents of the natural gas. After proper preliminary treatment, however, there seems to be no reason why this reagent should not be used for making reliable absorptions for the comparison of different samples of natural gas.

The average number of carbon atoms per molecule in the portion absorbed from each gas sample was computed from the composition of the residue and that of the original gas, which was found to be  $\text{CH}_4$ ,

74.1 per cent,  $\text{C}_2\text{H}_6$  — 25.7 per cent, and  $\text{N}_2$  — 0.2 per cent.

#### BEHAVIOR OF REAGENT TOWARD INDIVIDUAL PARAFFIN HYDROCARBONS

The assumption that gasoline vapors are more easily attacked by fuming sulfuric acid than the lower members of the paraffin series, such as methane and propane, seems to have been substantiated by the experiments that have just been described. It was found also that gasoline vapor was rapidly removed by fuming sulfuric acid from samples prepared by aspirating air through gasoline, a mixture containing 18.6 cc. of gasoline vapor showing a decrease of 10.6 cc. after 6 passages, 13.1 cc. after 12, 14.4 cc. after 18, and 15.6 cc. after 30 passages. These readings were made without the removal of fumes of sulfur dioxide. After 30 passages the gas was passed into a pipette containing potassium hydroxide and a further decrease of 1.9 cc. was obtained, giving a total absorption of 17.5 cc. for 30 passages. Thirty passages with nearly pure methane resulted in a decrease of about 2.0 cc. and with nearly pure ethane, a decrease of about 8.0 cc. was obtained for the same number of passages.

It is not possible, however, to obtain an accurate idea of the relative ease of attack of the different hydrocarbons by fuming sulfuric acid from the previous experiments since the various gases have not been dealt with in the pure condition, and the effect of the partial pressure of each constituent of a mixture upon the speed of its absorption must be taken into account. To obtain comparable data concerning the behavior of the reagent toward the individual paraffin hydrocarbons up to and including heptane in the paraffin series, an apparatus was devised in which all of the necessary operations might be effected at a temperature above the boiling point of heptane, 98.4° C.

A two-way stopcock was joined to the top of an old-style Orsat pipette and this modified pipette was connected to the tip of a jacketed Hempel burette by means of a twice bent capillary tube with a horizontal portion about 10 cm. long. A capillary side-arm carrying a stopcock was blown into the upright portion of the capillary tube a short distance above the top of the burette. The jacket of the burette was filled

with paraffin oil. The burette and the capillary tube that connected it with the pipette were heated to the desired temperature by passing an electric current through a resistance wire that was wound around the jacket and around the capillary tube over to the stopcock above the pipette. The pipette was housed in an asbestos oven with a sheet iron bottom and was heated by a Bunsen flame. The handle of the stopcock was passed through a small opening in the side wall of the oven so that it could be turned without disturbing the heating of the pipette.

In using the apparatus with liquid hydrocarbons, a small volume of a strong solution of potassium hydroxide was drawn in over the mercury which was employed in the burette, to effect the absorption of  $\text{SO}_2$  and  $\text{SO}_3$  which form a part of the gas mixture when it is drawn back into the burette. A small amount of the liquid hydrocarbon was next drawn in over the alkali and the temperature of the entire apparatus was then raised to about 120° C. The volume of gas that was formed by the complete conversion of the liquid hydrocarbon to the gaseous state was next read, the atmospheric pressure and the temperature of the paraffin oil in the jacket being noted at the same time, and the absorption was effected in the usual fashion by passing the gas back and forth from burette to pipette. Sufficient time must be allowed to elapse for the complete absorption of the  $\text{SO}_2$  and  $\text{SO}_3$  before the reading of the remaining volume is made, especially in the case of  $\text{SO}_3$  which is evolved in large quantities by the heating of the fuming sulfuric acid.

**ABSORPTION OF HEPTANE**—Two passages of a sample of heptane gas with a three-minute contact for each passage sufficed for the practically complete absorption of this hydrocarbon by fuming sulfuric acid. The small amount of residual gas did not disappear on cooling to room temperature and was probably air that had diffused through the reagent.

**ABSORPTION OF HEXANE, PENTANE AND ETHANE**—Thirty passages of a sample of hexane gas with an additional three-minute contact every six passages resulted in a decrease in volume of approximately 50 per cent. For pentane, the absorption under the same conditions amounted to approximately 35 per cent and for ethane, approximately 10 per cent.

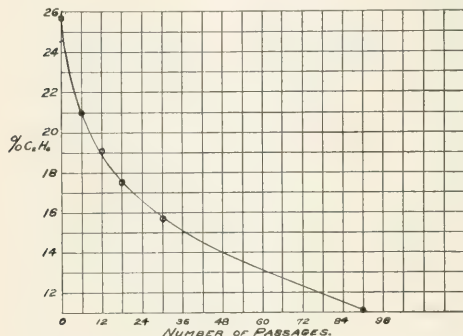
#### EFFECT OF TIME OF ABSORPTION UPON COMPOSITION OF RESIDUE

To determine the effect of the time of absorption upon the composition of the unabsorbed portion, different samples of the same natural gas were treated with fuming sulfuric acid for 6, 12, 18, and 90 times, respectively. Combustions were made on the residues and the results were computed to give apparent percentages of methane and ethane on the basis of the volume of the residue as the total volume. The percentages of ethane that were thus obtained were plotted against the number of passages as shown in the accompanying curve. The value used for 30 passages is the average of runs 4-10 from Table I.

The change in the composition of a sample of natural gas bearing gasoline vapors upon treatment with

fuming sulfuric acid is not proportional to the time of contact. This is to be expected when one considers the relatively small amount of gasoline vapors ordinarily present in samples of natural gas. In the case of the natural gas from which the data for the preceding curve were obtained, the change in composition obtained by 30 passages represents more than two-thirds that produced by 90 passages, and while this particular natural gas is not especially productive of gasoline, undoubtedly 30 passages of any sample of natural gas into fuming sulfuric acid would be sufficient to give data for the amount of gasoline vapor it carries.

COMPARISON OF RESIDUES AFTER TREATMENT WITH  $\text{H}_2\text{S}_2\text{O}_7$  AND AFTER REMOVAL OF GASOLINE ON A COMMERCIAL SCALE—In order to determine the usefulness



of the treatment of a sample of natural gas with fuming sulfuric acid as regards its availability for the production of gasoline, samples of natural gas were obtained from before and after the compressor at points where gasoline is being extracted from natural gas. These samples were analyzed and a portion of the sample from which the gasoline vapor had not been removed was treated with fuming sulfuric acid for 30 passages in the manner previously described, and then analyzed. The results that were obtained are shown in the following table:

TABLE II

	Natural gas I				Natural gas II			
Per cent	$\text{CH}_4$	$\text{C}_2\text{H}_6$	$\text{O}_2$	$\text{N}_2$	$\text{C}_2\text{H}_6$	$\text{C}_3\text{H}_8$	$\text{C}_4\text{H}_{10}$	$\text{O}_2$
Before compressor	58.9	40.0	0.0	1.1	41.5	21.8	7.6	29.1
After compressor	71.3	27.2	0.0	1.5	27.7	29.1	..	43.2
	(air)							
After treatment with $\text{H}_2\text{S}_2\text{O}_7$	78.0	18.3	0.9	2.8	25.4	23.4	..	11.0

Thirty passages through fuming sulfuric acid caused a decrease in volume of 9.8 per cent in natural gas I, and 30.0 per cent in natural gas II; the yield of gasoline was about 1 gallon 90° B. per 1000 cu. ft. from natural gas I, and about 5 gallons 97° B. per 1000 cu. ft. from natural gas II. In spite of the pronounced dissimilarity of the two samples, there seems to be a rather close agreement in the composition of the residues obtained by the commercial treatment of natural gas for the production of gasoline and by treatment of the natural gas with fuming sulfuric acid for thirty passages.

## SUMMARY

1—Fuming sulfuric acid exerts an appreciable absorbing action on certain samples of natural gas, the absorption increasing with the amount of gasoline vapors which the natural gas carries.

2—The average number of carbon and hydrogen atoms per molecule of hydrocarbon absorbed by fuming sulfuric acid (and thus the average molecular weight of the hydrocarbons) may be computed from the composition of the gas before and after absorption and from the decrease in volume that is obtained.

3—Application of this reagent to the study of natural gases for the production of gasoline may be made by determining the absorption under certain uniform conditions. It is desirable, however, to determine also the composition of the portion that is absorbed as a check upon the indications obtained by the decrease in volume.

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## THE DETERMINATION OF HYDROGEN IN GAS MIXTURES BY MEANS OF COLLOIDAL PALLADIUM

By G. A. BURRELL AND G. G. OBERPELL

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In this paper are reported results obtained by the authors, having to do with the use of a solution of sodium picrate and colloidal palladium for determining hydrogen in gas mixtures. Paal and Hartman<sup>1</sup> originated the method. Brunck<sup>2</sup> made an examination of it and recommended it.

In some of the authors' experiments the solution was prepared according to the direction of Paal and Hartman, as follows: 2 g. of sodium picrate and 2 g. of colloidal palladium were dissolved in 100 cc. of water. In other experiments the solution was prepared according to Brunck. He first makes a normal solution of sodium carbonate and neutralizes 5 g. of picric acid with 22 cc. of the solution, thereby producing about 5.6 g. of sodium picrate. He then dilutes the solution to 100 cc. with water and adds 2 g. of colloidal palladium. The life of the solution depends upon the presence of the unchanged reducible substance, the sodium picrate; hence by Brunck's method there is obtained a solution containing more sodium picrate and therefore of longer life. Colloidal palladium itself absorbs large volumes of hydrogen, but if used in the concentrated form it is costly. In the presence of an easily reducible substance, like sodium picrate, it acts only as a catalyst.

The solution is regenerated, after it has lost its absorbing power, as follows: The reagent is transferred from the gas pipette to a flask and much diluted sulfuric acid is added drop by drop to the solution so long as a precipitate results. A large excess of sulfuric acid is avoided because it might cause the colloidal palladium to change to the sulfate through the action of atmospheric oxygen. The precipitate is washed with water, which, although it may dissolve in some of the acid, carries no palladium into solution. The precipitate is then suspended in a small quantity of water and is

<sup>1</sup> Paal, C., and Hartman, W., "Gas Volumetric Determination of Hydrogen by Catalytic Absorption," *Ber. deutsch. chem. Gesell.*, **43** (1910), 243.

<sup>2</sup> Brunck, O., "Estimation of Hydrogen in Gas Mixtures," *Chem. Zeit.*, **1910**, No. 34, pp. 1313-1314, 1331-1332.

dissolved by adding sodium hydroxide drop by drop. Fresh sodium picrate is then added and the solution diluted with water to its original volume of about 100 cc. It is then again ready for use.

For use the authors place the reagent in an ordinary Orsat pipette filled with glass tubes and bring the gas mixture in contact with it by passing it back and forth between the pipette and gas burette until absorption is complete. The following table shows the results obtained when prepared mixtures of hydrogen and air were analyzed for their hydrogen content by means of the palladium solution:

RESULTS OF ANALYSES OF HYDROGEN-AIR MIXTURES

Sample No.	PER CENT HYDROGEN BY	
	Combustion in oxygen	Absorption in Pd solution
1	0.8	0.8
	0.8	0.8
	3.8	3.9
2	3.9	3.9
	28.2	28.3
3	28.2	28.3
	28.2	28.2
4	28.5	28.2
	28.6	28.6

The following analyses show the results obtained in analyzing the coal gas in Pittsburgh: By one method the carbon dioxide, illuminants, oxygen and carbon monoxide were removed by means of the usual absorbents, and the methane and hydrogen burned with oxygen in the slow-combustion pipette. By another method the carbon dioxide, illuminants, oxygen, and carbon monoxide were removed and then the hydrogen absorbed by the colloidal-palladium solution; the residual gas, methane and ethane were next burned in the slow-combustion pipette. In both cases nitrogen was estimated by difference. The second column shows the results obtained by the first method; the third column shows the results obtained by the second method; and the fourth column shows the results of the second column recalculated so as to make allowance for the ethane as determined by the second method. The third and fourth columns should correspond.

ANALYSES OF THE COAL GAS OF PITTSBURGH(a)

CONSTITUENTS	Without hydrogen absorption	With hydrogen absorption	Recalculated from Column 1 to include the ethane
CO <sub>2</sub> .....	2.4	2.3	2.4
Illuminants.....	8.7	8.7	8.7
O <sub>2</sub> .....	0.5	0.5	0.5
CO.....	11.8	11.4	11.8
CH <sub>4</sub> .....	37.5	35.0	35.3
C <sub>2</sub> H <sub>6</sub> .....		1.1	1.1
H <sub>2</sub> .....	35.3	35.8	36.4
N <sub>2</sub> .....	3.8	5.2	3.8
Total.....	100.0*	100.0	100.0

(a) The analysis was made over one year ago and is slightly different from some analyses of the Pittsburgh gas made recently.

Although the hydrogen results should correspond in Columns 2 and 3, the agreement is only fair.

There are given below other analyses made by the Bureau of Mines. In one column are shown analyses in which the hydrogen and methane were determined together by burning them with oxygen (indicated by a). In another column are shown the results obtained by absorbing the hydrogen with colloidal-palladium solution and then burning the methane in oxygen (indicated by b).

ANALYSES OF GAS MIXTURES BY TWO DIFFERENT METHODS									N <sub>2</sub>
No.	Method	CO <sub>2</sub>	Ill.	O <sub>2</sub>	CO	H <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	
5118	a	10.3	0.3	3.4	5.6	3.0	1.4	0.0	By difference
	b	10.6	0.2	3.5	5.6	3.0	1.5	0.0	
5094	a	7.5	0.1	7.4	5.2	2.9	1.2	0.0	
	b	7.4	0.3	7.7	5.6	3.0	1.1	0.0	
5052	a	9.6	0.5	1.0	9.7	5.3	2.3	0.0	
	b	9.6	0.6	1.1	9.5	5.6	2.4	0.0	
4862	a	9.0	0.2	6.4	5.1	2.2	1.2	0.0	
	b	9.0	0.1	6.6	5.2	2.4	1.3	0.0	
4837	a	8.2	0.6	6.6	5.2	3.0	1.0	0.0	
	b	8.1	0.6	6.4	5.4	3.3	1.2	0.0	
4725	a	5.3	0.0	12.1	3.6	1.5	0.8	0.0	
	b	5.5	0.0	12.0	3.3	1.7	0.7	0.0	

The above samples were collected in the experimental mine of the Bureau at Brucecon, Pa. They were automatically trapped in a special sampling device as the flame of an explosion traversed the entries of the mine.

The following sample was taken from the exhaust of a gasoline mine locomotive: A large number of these samples were gathered to study the composition of the exhaust gases under different conditions of usage of the motor. It should be added that this sample was collected under particularly bad conditions of motor usage. The analysis marked a was made by absorbing the carbon dioxide in caustic-potash solution, the illuminants in bromine water, the oxygen in alkaline pyrogallate solution, and the carbon monoxide in ammoniacal cuprous-chloride solution; the methane and hydrogen were then determined by burning in oxygen and the nitrogen estimated by difference. The analysis marked b was made in the same manner except that after the other absorbable gases had been removed the hydrogen was absorbed by colloidal palladium and the methane burned in oxygen.

ANALYSES OF EXHAUST GASES OF A GASOLINE MINE LOCOMOTIVE

No.	Method	CO <sub>2</sub>	Ill.	O <sub>2</sub>	CO	H <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	N <sub>2</sub>
4280	a	5.9	0.3	1.0	13.3	8.7	0.8	0.0	70.0
	b	5.9	0.2	0.8	13.1	8.6	0.8	0.0	70.6

In the analysis of complex mixtures Paal and Hartman recommend that carbon dioxide, unsaturated hydrocarbons, oxygen and carbon monoxide be first removed before absorbing the hydrogen by the palladium solution. They state that carbon monoxide seems to retard the catalytic effect in that it slows the reaction. They say that oxygen must be removed because oxygen and hydrogen combine in the presence of the palladium and they found that ethylene and hydrogen form ethane in the presence of the palladium solution, and that even if unsaturated hydrocarbons be absent, or present only in negligible quantities, the gas mixture must be treated with bromine water, as such treatment frees the mixture of possible traces of sulfur, phosphorus and arsenic compounds, which, even in traces, retard the catalytic effect.

A solution which the authors of this paper prepared removed 11.3 cc. of hydrogen per cc. of solution before it became too sluggish to use. Theoretically, 1 cc. of the solution should absorb about 40 cc. of hydrogen. Long before this theoretical quantity is obtained, however, the solution becomes sluggish in its action. In analyzing mixtures of hydrogen and air prepared in the laboratory it was found that from 6 to 25 minutes were required to remove the hydrogen from mixtures containing from 0.8 to 30 per cent. To remove the hydrogen from coal gas, exhaust gases from gasoline locomotives, and from



gases collected during explosions in mines, a maximum of 30 minutes was required. All determinations were made by simply passing the gas mixture back and forth into an Orsat pipette containing the solution and provided with glass tubes. The removal of the hydrogen probably should be performed faster if the latter were shaken with the reagent as in a Hempel pipette. The colloidal palladium was obtained by the Bureau from Kalle & Company, Germany: 6 g. cost \$15.84.

In the authors' opinion the advantage of the method over the use of palladium asbestos or palladium sponge is in the fact that it never fails in the authors' experience to work satisfactorily—something that, in the authors' experience, cannot be said regarding the use of the former substances.<sup>1</sup> In addition, it can be placed in an ordinary pipette of a gas-analysis apparatus and does not have to be heated in order to excite it to action. Its disadvantage lies in its slowness of action and the somewhat troublesome method of regeneration of the used material.

Hempel<sup>2</sup> states that the solution slowly loses its absorbing power even in the dark. He recommends that for each analysis small quantities of the freshly prepared liquid be used over mercury. The authors, however, have in satisfactory use at the present time one solution that was prepared in January of this year. The pipette has been surrounded with black paper.

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## IODINE NUMBER OF LINSEED AND PETROLEUM OILS<sup>3</sup>

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The linseed oil used in the manufacture of printing ink is of the so-called "burnt" type. There are two general processes for its manufacture—one in which the oil is heated until the vapors take fire and continue to burn, the oil being allowed to burn until it attains the desired viscosity; and a second in which the oil is heated without permitting it to take fire.

Burnt oil is prepared in several grades, all differing from the raw oil in an increase of viscosity, specific gravity, and acid number, and a decrease in the iodine number. The longer the oil is heated the greater these differences become.

In the determination of the iodine value of some burnt linseed oils difficulty was experienced in obtaining concordant results. Leeds<sup>4</sup> has published some figures for iodine absorption of lithographic oils. Kitt<sup>5</sup> has also published a series of results which show decrease in iodine absorption with increasing viscosity, but the figures do not agree with those given by Leeds; their determinations were made according to the Hübl method.<sup>6</sup> In recent years this method has been so generally replaced by the rapid and more convenient

Hanus<sup>1</sup> method that it was considered desirable to learn the values afforded by this method. Preliminary work showed that small variations in the method employed produced varying results. It has been well established that iodine absorption includes not only the halogen taken up by unsaturated compounds, but that the substitution of halogen for hydrogen with the formation of halogen acid occurs simultaneously. Various methods for determining the amount of substitution have been suggested, with the view of obtaining a corrected value which would represent the addition only, but very little use has been made of them. It has been generally recognized that an excess of iodine is necessary, and it has been assumed that all oils are alike in the amount of excess required. The appended results obtained by us show that this is far from being true. Various quantities of iodine have been suggested as the proper excess which should be present, but practically all of these are given in connection with discussions of the Hübl method, and may not hold true for the Hanus method. Furthermore, there has been a lack of uniformity in the use of the term "excess of iodine." In the following tables this expression is used to mean that percentage of the total amount added which remains unchanged at the expiration of the time allowed for absorption.

### PROCEDURE

The method employed was essentially the modification of the Hanus method suggested by Hunt.<sup>2</sup> Thirteen and two-tenths grams of iodine were dissolved in 1 liter of glacial acetic acid (99.9 per cent), and 3 cc. of bromine added. This solution was always allowed to stand for some days before being used. The thio-sulfate solution employed was approximately tenth normal, and was standardized by means of potassium bichromate. Standardization was repeated at frequent intervals. A freshly prepared starch solution was used; also a 10 per cent solution of potassium iodide, prepared in small amounts and kept in a brown bottle. The temperature of the room was maintained at 25° C. to prevent variations caused by change of temperature. The reagents were of standard quality and errors caused by impurities were eliminated by running blanks with each series of determinations. When it was desired to use like amounts of an oil in a series of tests, 4 g. of the oil were dissolved in chloroform in a 200 cc. graduated flask and the solution allowed to reach room temperature. Ten cc. portions of this solution, representing 0.2 g. of oil, were measured from a burette. The general procedure was as follows: The exact weight of oil was transferred to 250 to 300 cc. glass-stoppered Jena bottles; the required amount of Hanus solution was added from a burette. The mixture was allowed to stand for exactly 30 minutes in a dark closet; 25 cc. of the 10 per cent potassium iodide solution and 100 cc. of water<sup>3</sup> were added,<sup>4</sup> and the excess of iodine was immediately titrated with thio-sulfate.

<sup>1</sup> G. B. Taylor states, however, that the colloidal palladium solution does not work satisfactorily on gases obtained by distilling coal at low temperatures. See THIS JOURNAL, Oct., 1914, p. 845.

<sup>2</sup> Hempel, Walther, "Contribution to the Determination of Hydrogen and Methane in Gas Mixtures," *Z. angew. Chem.*, **25** (1912), 1841.

<sup>3</sup> Published by permission of the Director of the Bureau of Standards. *J. Soc. Chem. Ind.*, **13** (1894), 203.

<sup>4</sup> *Chem. Rev. Fett. u. Harz Ind.*, **8** (1901), 40; *J. Soc. Chem. Ind.*, **20** (1901), 40.

<sup>5</sup> Dingle's *Poly. J.*, **253**, p. 281; *J. Soc. Chem. Ind.*, **3** (1884), 641.

<sup>1</sup> *Z. Untersuch. Nahr. Genussm.*, **20** (1901), 913; *J. Soc. Chem. Ind.*, **20** (1901), 1246.

<sup>2</sup> *J. Soc. Chem. Ind.*, **21** (1902), 454.

<sup>3</sup> Tolman and Munson, *J. Am. Chem. Soc.*, **25** (1903), 244.

<sup>4</sup> Gill, "Oil Analysis," 6th ed., p. 62, footnote

The factors known to influence the iodine number are the temperature, the time of absorption, the weight of oil taken, and the excess of iodine present obtained by increasing the amount of iodine solution. The exact effect of each factor was studied by varying one at a time, this procedure being followed with a series of oils.

#### SAMPLES

The samples employed were as follows:

I—A raw linseed oil, Sample No. 3, of the four linseed oils tested by the American Society for Testing Materials<sup>1</sup> in 1909. This sample had been hermetically sealed, immediately upon completion of the tests in 1909, and had been kept in a cool, dark closet.

II—A boiled oil of the so-called "bung-hole" variety.

III—Four burnt linseed oils, Nos. 00, 1, 3, and 5. These oils were obtained from northwestern seed and, after refining, were heated in copper kettles at a temperature of 560 to 600° F., until the desired consistency was attained.

IV—Three petroleum oils. Two of these, marked Light Oil No. 1 and No. 2, were automobile cylinder oils, and the third was an engine oil. Upon analysis these oils gave the following figures:

	B. S. eng.	Light No. 1	Light No. 2
Flash.....	175°	220°	230°
Fire.....	210	265	280
Sp. gr. 20°/4°.....	0.9260	0.8738	0.9265
Carbonization (3 hrs. at 250°), per cent.....	1.01	0.11	0.23
Oxygen absorb. 144½ hrs., per cent.....	1.60	1.91	1.90
Original acidity (mg. KOH, per g.).....	0.70	0.08	0.17
Acidity after exposure.....	13.52	14.39	13.83
Increase in acidity.....	12.82	14.31	13.66

The other constants of the samples were not determined, as they have no bearing on the present problem.

#### DISCUSSION OF RESULTS

Table I, the results of which are plotted in Figs. 1 and 2, shows the difference in behavior of the various linseed oils when the amount of iodine solution added is kept constant and the weight of oil is varied. Fig. 1 shows the change in iodine number with increasing amounts of oil. The curves in Fig. 2 have been calculated from the data given in Table I to represent the change in iodine number with a decrease in the excess of iodine present. It will be of interest to compare these curves with those in Fig. 3. The striking point in this connection is the range in weight of oil over which the iodine number is constant in the raw and boiled oils, as compared with that of the burnt oils. It will be seen that, contrary to the general opinion, the oil with the highest iodine number does not require the largest excess of iodine to reach a maximum absorption value. It is not desirable to work with less than 0.1 g. of oil, because of the difficulty in obtaining constant values. Between 0.1 and 0.2 g. small variations in weight are negligible in raw and boiled oils, but are important in the burnt oils.

It is apparent that substitution plays an important part in the reaction, and we shall refer to this point later on.

<sup>1</sup> See report of Committee E on Preservative Coatings for Structural Materials, Proceedings of the A. S. T. M., 9 (1909), 184; analyses by J. B. Tuttle. Another sample of this same oil was also tested in 1911, results of which are given in report of Subcommittee E of Committee D-1, Proceedings of the A. S. T. M., 11 (1911), 23-30.

TABLE I—LINSEED OIL. WEIGHT OF IODINE SOLUTION VARIED  
Temperature—25° C., Time—30 minutes; Hanus solution—25 cc.

Grams Iodine					Grams Iodine				
Grams oil	Ad-ded	Ab-sorbed	Iodine No.	Average	Grams oil	Ad-ded	Ab-sorbed	Iodine No.	Average
A—RAW OIL					B—BOILED OIL				
0.0522	0.6669	0.0962	184.3	...	0.0600	0.6902	0.1066	177.6	...
0.0522	0.6669	0.0970	185.8	...	0.1181	0.6902	0.2102	178.0	...
0.0522	0.6669	0.0967	185.3	185.1	0.1322	0.6902	0.2355	178.3	...
0.1044	0.6669	0.1949	187.3	...	0.1673	0.6902	0.2984	178.3	...
0.1044	0.6669	0.1955	187.3	...	0.2061	0.6902	0.3682	178.5	...
0.1566	0.6669	0.2912	186.0	...	0.2220	0.6902	0.3962	178.4	...
0.1566	0.6669	0.2906	185.6	...	0.2523	0.6902	0.4438	175.7	...
0.1514	0.6669	0.2844	187.8	186.5	0.2783	0.6902	0.4832	173.7	...
0.2004	0.6669	0.3735	186.4	...	0.2920	0.6902	0.4976	170.4	...
0.2004	0.6669	0.3746	186.4	186.4	0.3217	0.6902	0.5250	163.2	...
0.2504	0.6669	0.4543	181.5	...	0.3378	0.6902	0.5346	160.6	...
0.2504	0.6669	0.4572	182.6	182.1	0.3583	0.6902	0.5518	154.0	...
0.3027	0.6669	0.5098	168.4	...	0.3874	0.6902	0.5744	148.2	...
0.3027	0.6669	0.5098	168.4	168.4	0.3969	0.6902	0.5848	147.4	...
0.4342	0.6669	0.5889	129.2	...	0.5550	0.6902	0.6344	144.0	...
0.4342	0.6669	0.5888	129.6	129.4	D—BURNT LINSEED OIL NO. 1				
0.5008	0.6669	0.6103	121.2	121.5	0.0880	0.6787	0.1220	138.6	138.6
0.5008	0.6669	0.6103	121.2	121.5	0.1891	0.6787	0.2480	131.1	...
0.6054	0.6669	0.6091	106.0	106.0	0.1917	0.6787	0.2512	131.0	131.0
0.8013	0.6669	0.6191	77.3	77.3	0.2856	0.6787	0.3310	115.9	115.9
C—BURNT LINSEED OIL NO. 00					0.3577	0.6787	0.7788	105.9	...
0.1235	0.6811	0.1827	148.0	...	0.3595	0.6787	0.7396	105.6	105.6
0.1268	0.6811	0.1828	148.4	148.2	0.4377	0.6787	0.9195	95.8	95.8
0.1465	0.6811	0.2154	147.0	147.0	0.5853	0.6787	0.9753	81.2	81.2
0.1842	0.6811	0.2616	142.0	...	F—BURNT LINSEED OIL NO. 5				
0.1863	0.6811	0.2632	141.3	141.7	0.0517	0.5874	0.0668	129.2	...
0.2539	0.6779	0.3401	133.0	...	0.0517	0.5874	0.0682	131.9	130.4
0.2506	0.6779	0.3297	131.6	132.3	0.1034	0.5874	0.1336	129.2	...
0.3248	0.6779	0.4128	118.3	...	0.1034	0.5874	0.1325	128.5	...
0.3362	0.6779	0.4171	117.1	117.7	0.1034	0.5874	0.1325	128.1	128.6
0.4490	0.6779	0.4658	103.7	...	0.1551	0.5874	0.1858	119.8	...
0.4497	0.6779	0.4658	103.6	103.6	0.1551	0.5874	0.1858	119.8	119.8
0.6058	0.6779	0.5216	86.1	86.1	0.2054	0.5860	0.2213	107.7	...
0.7831	0.6779	0.5583	71.3	71.3	0.2054	0.5880	0.2234	108.8	108.3
E—BURNT LINSEED OIL NO. 3					0.2423	0.5870	0.2468	101.7	101.8
0.1085	0.5846	0.1412	130.1	...	0.2423	0.5870	0.2464	101.7	101.8
0.1085	0.5846	0.1406	129.6	129.9	0.2826	0.5870	0.2671	94.5	...
0.1632	0.5846	0.1948	119.4	119.8	0.2826	0.5870	0.2680	94.6	94.6
0.2376	0.5846	0.2463	103.7	...	0.3634	0.5870	0.3016	83.0	83.0
0.2376	0.5846	0.2463	103.7	103.7	0.4108	0.5860	0.3613	77.2	77.2
0.3264	0.5846	0.2937	90.1	90.1	0.4108	0.5860	0.3717	77.6	77.4
0.3264	0.5846	0.2944	90.2	90.2	0.5249	0.5870	0.2883	60.6	60.6
0.4158	0.5846	0.3313	79.7	79.7	0.6162	0.5860	0.3181	60.2	...
0.5346	0.5846	0.3616	67.6	67.6	0.6162	0.5860	0.3688	59.9	60.0
0.6534	0.5846	0.3883	59.4	59.4	0.7268	0.5870	0.3810	52.4	52.4

Table II, in which the amount of Hanus solution is varied, is plotted in Fig. 3. Even more clearly than Fig. 2 does this show that burnt linseed oils do not readily reach a maximum.

TABLE II—LINSEED OIL. AMOUNT OF HANUS SOLUTION VARIED  
Temperature—25° C.; Oil—0.2 gram; Time—30 minutes

Hanus sol.	Cc. Grams Iodine Ad-ded	Iodine Ab-sorbed	Iodine No.	Average	Hanus sol.	Cc. Grams Iodine Ad-ded	Iodine Ab-sorbed	Iodine No.	Average
A—RAW OIL					B—BOILED OIL				
20	0.4737	0.3258	162.9	...	20	0.5522	0.3490	174.5	...
20	0.4737	0.3271	163.6	...	20	0.5522	0.3472	173.9	174.2
20	0.4737	0.3266	163.3	163.6	25	0.6902	0.3580	179.0	...
25	0.5928	0.3619	181.0	...	25	0.6902	0.3574	178.7	...
25	0.5928	0.3615	180.8	...	25	0.6902	0.3560	178.0	178.6
25	0.5928	0.3609	180.5	180.8	30	0.8282	0.3606	180.3	...
30	0.7114	0.3747	187.4	...	30	0.8282	0.3606	180.3	...
30	0.7114	0.3754	187.7	187.6	30	0.8282	0.3596	179.8	180.1
35	0.8300	0.3822	191.1	...	35	0.9662	0.3617	180.8	...
35	0.8300	0.3820	191.0	...	35	0.9662	0.3617	180.8	180.8
35	0.8300	0.3816	190.8	191.0	40	1.1044	0.3619	180.7	...
40	0.9486	0.3831	191.6	...	40	1.1044	0.3619	180.9	...
40	0.9486	0.3806	190.3	191.0	40	1.1044	0.3634	181.7	181.1
50	1.1862	0.3832	191.6	191.6	40	1.1862	0.3634	181.7	181.1
60	1.4235	0.3840	192.0	...	50	1.3759	0.3639	181.9	181.9
60	1.4235	0.3824	191.2	191.6	60	1.6510	0.3625	181.2	...
75	1.7793	0.3846	192.4	192.4	60	1.6510	0.3630	181.5	181.3
75	1.7793	0.3828	191.4	191.8	D—BURNT OIL NO. 3				
C—BURNT OIL NO. 00					20	0.4622	0.1940	97.0	...
20	0.5408	0.2640	132.0	...	20	0.4622	0.1932	96.6	96.8
20	0.5408	0.2623	131.0	131.6	25	0.5778	0.2128	106.4	...
25	0.6760	0.2840	141.0	...	25	0.5778	0.2125	106.6	...
25	0.6760	0.2812	140.6	140.8	25	0.5778	0.2152	107.6	107.2
30	0.8112	0.2992	149.6	...	30	0.6933	0.2284	114.2	...
30	0.8112	0.2940	147.0	148.3	30	0.6933	0.2282	114.1	114.1
30	0.8112	0.2906	144.8	149.8	35	0.9244	0.2444	122.2	...
40	1.0816	0.2980	149.0	149.4	40	0.9244	0.2432	121.6	121.9
50	1.3520	0.3054	152.7	...	50	1.1556	0.2488	124.4	...
50	1.3520	0.3054	152.2	152.4	50	1.1556	0.2488	124.4	124.4
60	1.6224	0.3056	152.6	152.6	60	1.3866	0.2518	125.9	...
70	2.0280	0.3066	153.3	...	60	1.3866	0.2506	125.3	125.6
70	2.0280	0.3060	153.0	153.1	75	1.7334	0.2514	125.7	...
E—BURNT OIL NO. 5					75	1.7334	0.2506	125.3	125.5
20	0.4688	0.1904	98.3	...	F—BURNT OIL NO. 5(0)				
20	0.4688	0.1950	97.5	97.9	20	0.4688	0.1804	90.2	...
25	0.5860	0.2148	107.4	...	20	0.4688	0.1800	90.0	90.1
25	0.5860	0.2140	107.0	107.2	25	0.5860	0.1962	98.1	97.7
35	0.8204	0.2440	121.0	...	35	0.8204	0.2148	107.4	...
35	0.8204	0.2424	121.2	121.6	35	0.8204	0.2094	104.7	106.0
50	1.1720	0.2602	130.1	...	50	1.1720	0.2218	110.9	...
50	1.1720	0.2584	129.2	129.6	50	1.1720	0.2186	109.3	110.1

The factor "excess of iodine" may be varied by changing the weight of oil or the amount of Hanus solution. In either case the effect upon the iodine number is about the same.

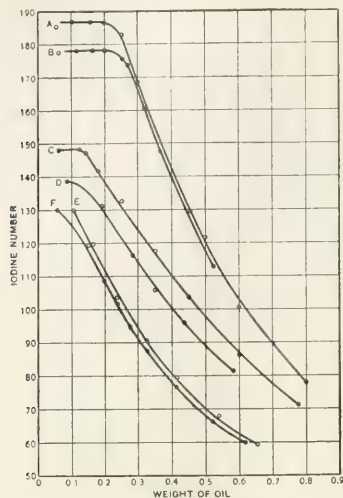


FIG. 1—WEIGHT OF OIL VARIED

It is not sufficient, however, merely to specify the percentage excess of iodine, as the following iodine values, taken from Tables I and II, will show:

OIL	Average iodine numbers	
	on 0.1 g. oil and 25 cc. Hanus sol.	on 0.2 g. oil and 50 cc. Hanus sol.
Raw.....	186.4	191.6
Boiled.....	178.5	181.9
No. 00.....	139.5	152.4
No. 3.....	111.0	124.4
No. 5.....	109.0	129.6

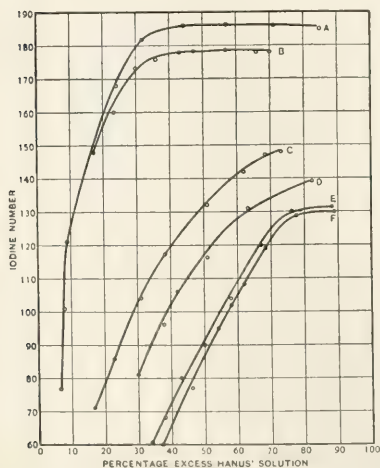


FIG. 2—WEIGHT OF OIL VARIED

These figures, together with the results shown in Tables I and II, demonstrate clearly that in these oils,

at least, an iodine number should always be accompanied by full data as to the conditions under which it is determined, in order that it may be used for comparison.

When dealing with unknown oils it will probably be found satisfactory to determine the iodine value for several weights of oil, other conditions being held constant. For convenience we would recommend the use of 25 cc. of Hanus solution and 30 minutes' absorption. When testing for the purity of a sample of oil any sample of unknown purity could be used as a standard, when by determining the iodine number on both samples under identical conditions adulteration or inferior quality should be readily detected.

The curve for Table II—F will be found on Fig. 6, and will be referred to later. It is placed there so as to contrast it with the results given in Table II—E.

TABLE III LINSEED OIL. TIME OF ABSORPTION VARIED  
Temperature—25° C., 0.2 g. oil; Hanus solution—25 cc.

Time Min.	Grams Ad-ded	Iodine Ab-sorbed	Iodine No.	Average	Time Min.	Grams Ad-ded	Iodine Ab-sorbed	Iodine No.	Average
A—RAW OIL					E—BURNED LINSEED OIL NO. 1				
5	0.5972	0.3284	164.2		5	0.5746	0.2310	115.5	115.5
5	0.5972	0.3281	164.1	164.2	5	0.5746	0.2405	120.3	
15	0.5972	0.3497	174.9		15	0.5746	0.2436	121.8	
15	0.5972	0.3493	174.7	174.8	15	0.5746	0.2405	120.3	
30	0.5972	0.3629	181.5		15	0.5746	0.2440	122.0	
30	0.5972	0.3625	181.3		15	0.5746	0.2426	121.3	121.1
30	0.5972	0.3616	180.8	181.2	30	0.5746	0.2500	125.0	
45	0.5972	0.3677	183.9		30	0.5746	0.2497	124.9	
45	0.5972	0.3680	184.0	184.0	30	0.5745	0.2493	124.7	
60	0.5972	0.3737	186.9		30	0.5746	0.2496	124.8	124.9
60	0.5972	0.3736	186.8		45	0.5746	0.2540	127.0	
60	0.5972	0.3733	186.7	186.8	45	0.5746	0.2519	126.0	
B—BOILED OIL					45	0.5746	0.2525	126.3	126.4
5	0.6811	0.3380	169.0		60	0.5746	0.2540	127.0	
5	0.6811	0.3342	167.1	168.0	60	0.5746	0.2552	127.6	
15	0.6811	0.3518	175.9		60	0.5746	0.2559	128.0	127.6
15	0.6811	0.3510	175.5		F—BURNED LINSEED OIL NO. 3				
15	0.6811	0.3508	175.4	175.6	5	0.6691	0.2252	112.6	112.6
20	0.6811	0.3548	177.4	177.4	15	0.6691	0.2394	119.7	
30	0.6811	0.3556	177.8	177.8	15	0.6691	0.2374	118.7	
45	0.6811	0.3600	180.0		15	0.6691	0.2402	120.1	
45	0.6811	0.3602	180.1	180.0	15	0.6691	0.2367	118.4	119.2
60	0.6811	0.3592	179.6	179.9	30	0.6691	0.2472	123.6	
C—BOILED OIL (a)					30	0.6691	0.2483	124.2	
5	0.6760	0.3282	164.1		30	0.6691	0.2480	124.0	123.9
5	0.6760	0.3266	163.3	163.7	45	0.6691	0.2532	126.6	
10	0.6760	0.3422	171.1		45	0.6691	0.2525	126.3	126.5
10	0.6760	0.3402	170.1	170.6	60	0.6691	0.2539	127.0	
15	0.6760	0.3466	173.3		60	0.6691	0.2539	127.0	
15	0.6760	0.3462	173.1	173.2	60	0.6691	0.2542	127.1	127.0
30	0.6760	0.3490	174.5		G—BURNED LINSEED OIL NO. 5				
30	0.6760	0.3506	175.3	174.9	5	0.6689	0.2145	107.3	
45	0.6760	0.3528	176.4	176.4	5	0.6689	0.2118	105.9	
60	0.6760	0.3528	176.4		5	0.6689	0.2136	106.8	106.5
60	0.6760	0.3518	175.9	176.2	15	0.6689	0.2309	116.9	
D—BURNED LINSEED OIL NO. 00					15	0.6689	0.2271	115.0	
5	0.5606	0.2405	120.3		15	0.6689	0.2271	115.0	115.5
5	0.5606	0.2509	125.5		30	0.6689	0.2390	119.5	
15	0.5606	0.2495	124.8		30	0.6689	0.2390	119.5	119.5
15	0.5606	0.2486	124.3		45	0.6689	0.2411	120.6	
15	0.5606	0.2501	125.1	124.9	45	0.6689	0.2411	120.6	
30	0.5606	0.2584	129.2		45	0.6689	0.2425	121.3	120.8
30	0.5606	0.2579	129.0	129.1	60	0.6689	0.2432	121.6	
45	0.5606	0.2607	130.4		60	0.6689	0.2432	121.6	121.6
45	0.5606	0.2593	129.7		(a) Temperature 0°.				
45	0.5606	0.2586	129.3	129.8					
60	0.5606	0.2635	131.8						
60	0.5606	0.2614	130.7						
60	0.5606	0.2642	132.1						
60	0.5606	0.2628	131.4	131.5					

Table III (omitting C) is plotted in Fig. 4. The curves show that after the first five minutes the absorption is slow, and the difference of a few minutes one way or the other after 15 minutes, will have little effect on the iodine value; 30 minutes should prove a very satisfactory time and is now generally adopted.

Figs. 5 and 6 contain two sets of curves showing the effect of temperature. Table III—B and C show that, other conditions being equal, small differences in tem-



perature at which an iodine value is obtained are negligible, so far as boiled oils are concerned, and presumably raw oils also, since their behavior is very much like that of the former. This is not, however, true of the burnt linseed oils, as inspection of the curves for Table II—E and F will readily show. Using the largest practical excess of iodine, the difference between the results obtained at the two temperatures is too great to be considered negligible. Moreover, the fact that the curves are not even approximately parallel makes it difficult to allow for differences in temperature.

It will be seen that about 90 per cent of the absorption occurs in the first 5 minutes. If we assume that the addition of iodine is nearly instantaneous, and the substitution that part of the reaction which continues over a wide range of time, it is evident that any lessening of the time of absorption, which will at best

played for the determination, with 25 cc. of the iodine solution.

TABLE IV PETROLEUM OILS TIME VARIED  
Temperature—25° C.; Hanus solution—25 cc.

TIME 30 MINUTES			TIME—3 HOURS		
Grams oil	Grams I iodine absorbed No.		Grams oil	Grams I iodine absorbed No.	
A—LIGHT OIL, NO. 1					
0.2313	0.0683	29.5	0.0202	0.0167	77.9
0.5896	0.1454	24.7	0.0418	0.0307	69.4
0.7542	0.1756	23.3	0.0644	0.0448	65.7
0.9222	0.2006	21.8	0.1312	0.0735	52.9
1.0322	0.2105	20.4	0.1683	0.0870	48.8
1.5037	0.2621	17.4	0.1932	0.0953	46.6
2.3203	0.3288	14.2	1.009	0.2202	21.9
B—LIGHT OIL, NO. 2					
0.2381	0.0807	33.9	1.059	0.2235	21.1
0.5144	0.1363	26.5	1.203	0.2423	20.1
0.6800	0.1678	24.6	1.305	0.2516	19.3
1.0288	0.2145	20.9	2.069	0.3058	14.8
1.6731	0.2819	16.9			
2.5151	0.3429	13.6			
C—ENGINE OIL					
D—ENGINE OIL					
E—ENGINE OIL					

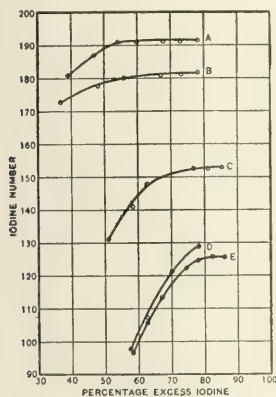


FIG. 3—AMOUNT OF HANUS' SOLUTION VARIED

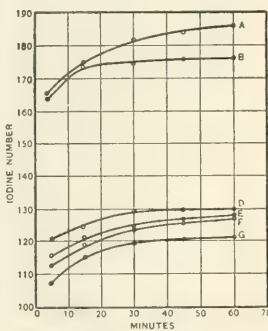


FIG. 4—TIME OF ABSORPTION VARIED

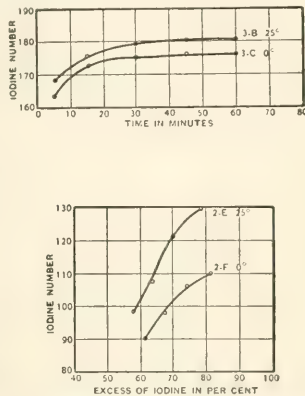


FIG. 5 (above)—TIME AND TEMPERATURE VARIED

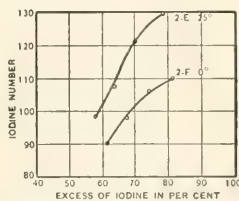


FIG. 6—TEMPERATURE AND EXCESS IODINE VARIED

eliminate only a small part of the total substitution, may give low values which properly belong on the portion of the curve which is rapidly changing its slope.

A study of the effect of temperature on substitution is a more promising field than that of the time factor. Table II—E and F, as plotted in Fig. 6, show that at the lower temperature the effect of increasing the excess of iodine is less than at the higher one. The difference in the iodine values between 15 and 30 minutes is about 5 units (see Fig. 4), whereas the difference between 25° C. and 0° C. at the maximum percentage excess of iodine employed, is 20 units (see Fig. 6).

Table IV (Fig. 7) shows clearly the futility of attempting to reach a constant value for mineral oils by increasing the excess of iodine. For the smaller quantities of oil used in the determination slight changes in the amount of oil taken cause large differences in the iodine number. Undoubtedly the lower values are more nearly correct than the higher ones, and therefore increasing the excess of iodine increases materially the error involved. To obtain concordant results the weight of oil and amount of iodine solution must be defined within very narrow limits. Our results indicate that not less than 1 g. of oil should be em-

approach a constant value with a decreasing weight of oil, or increasing excess of iodine, while, on the contrary, the latter tend to approach a constant value with increasing weight of oil.

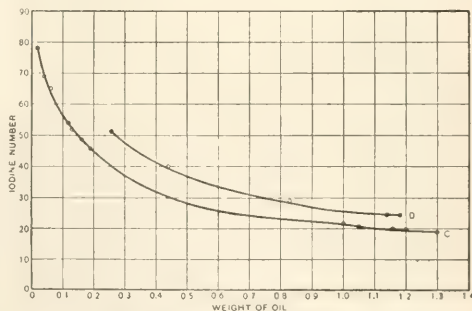


FIG. 7—WEIGHT OF ENGINE OIL VARIED

#### SUMMARY

The iodine values of raw, boiled, and burnt linseed oils were determined by the Hanus method, varying widely the amounts of oil and iodine used and the time of absorption.

It is shown that in order to obtain concordant results for iodine absorption a prescribed procedure must be followed exactly.

To obtain comparable results a standard procedure should be adopted in which the limits are more exactly defined than is true at present. This is particularly necessary in the case of burnt linseed oils. With raw linseed oil a constant value is reached within comparatively wide limits of weight of oil and excess of iodine.

A study was made of the effect of temperature on the iodine absorption, from which it would appear that it may be feasible to improve the Hanus method by working at lower temperatures than those which have been used, and thus eliminate part of the substitution which occurs simultaneously with the addition.

The results obtained show that when used under exact conditions the Hanus method is to be recommended for simplicity of preparation of the solutions employed, ease of manipulation, and for concordance of results obtained.

Suggestions are made for the standardization of the method of determining the iodine number of mineral oils. The necessity for such action is shown by the results on several samples of lubricating oils.

We wish to express our appreciation of the courtesy of Messrs. Ault & Wiborg, of Cincinnati, in furnishing us with the burnt linseed oils used in this work.

BUREAU OF STANDARDS, WASHINGTON, D. C.

### EGG ALBUMIN IN BAKING POWDER

By H. LOUIS JACKSON

Received August 3, 1914

This paper is a summary of the results of three series of comparative baking tests, using different baking powders with and without egg albumin.

They were carried out in the following bakeries in the city of Boise, Idaho:

1—On cup cakes, during July and August, in the Home Bakery, and completed Sept. 4th, 1913.

2—On biscuits, April 23rd to May 15th, by the Shaeffer Baking Company.

3—On biscuits, June 18th to June 24th, in the Imperial Bakery.

Calculations for the last two were finished June 27th, 1914.

In all the bakings, the egg albumin added to the powders was always Merck's "Albumin, Egg, Impalp. Powder Soluble;" it was added as described in Series II. The cup cakes or biscuits were the bakers' regular commercial mixture. The ingredients, manipulation, time of baking, and all other factors were left to his professional judgment and skill with the exceptions of the baking powder and the oven temperature. At the time of mixing the baker was furnished the proper amount of baking powder, weighed to a tenth of a gram. Further details as to the powders are given under each series. The temperature was that regularly used in each bakery, except in the third series, when progressively lower temperatures were employed in order to study the effects of unfavorable conditions.

High and low temperatures are defined as follows by A. J. Stephan, of the Imperial Bakery, the largest in the city: bread requires the highest temperature, baking best at about 500° F. (260° C.); 425° F. (218½° C.) is the lowest possible for bread, as at this temperature it dries out too much. The highest temperature that can be used is 520° F. (271.1° C.). Pies are baked at 450° to 500° F. (232.2°–260° C.). Cakes, according to kind, at 350° to 450° F. (176.7–232.2° C.). Biscuits require for best results about 490–500° F. (254.4–260° C.); 425° F. (218.3° C.) is considered the lowest that should be used for biscuits, though they will bake poorly at 400° F. (204.4° C.).

The temperature in the first series was not known, as the oven contained no thermometer. All products were judged by the bakers as soon as expedient after removal from the oven. The judgment of the bakers must be regarded as unbiased as, at this writing, they are still ignorant of the manipulations to which the baking powders were subjected. Products were weighed and measured as soon as they had cooled to room temperature, unless otherwise stated.

A Bureau of Standards cylindrical brass liter was half filled with sifted rape seed (through 16), jarred in a uniform manner, the filling completed and jarred as before, filled to overflowing and the excess struck off with a straight edge. The seeds were then poured into a tared vessel, weighed to the nearest half gram in the first series, and to the nearest tenth of a gram in the second and third series. The cakes or biscuits were weighed in a like manner, weighing and measuring two, three, or four at a time, as two, three, or four could be introduced into the liter measure without touching each other. Cakes or biscuits were placed in the liter, one at a time, entirely surrounded by seed, and so on, until the vessel was filled, jarring it in the same manner as before, every care being taken to make this a very uniform procedure. The difference between the first and second weights of seed is that displaced by the biscuits. The intent was to make all measurements so numerous that the unavoidable errors in measurement would be averaged out in the final result. The average weight of 1,000 cc. of seed was found for each baking and is usually the average of ten weighings, though in the first series, three, five, six, eight and nine weighings were averaged together for different bakings.

#### SERIES I

Cup cakes were chosen because in the estimation of the bakers they were best adapted to experiment. The bakers knew this product so thoroughly that they were confident they could detect any change in its appearance. A cream of tartar powder (Cleveland's) was used because it was the only one used in this bakery, and it was not desired to change the nature of their cake in any way, as part of each baking was to supply the regular trade.

Objection may be made that fresh eggs were used as an ingredient in the cakes of the first series, but it

must be remembered that most products baked contain eggs, except in baking powder biscuits.

The method of calculation follows:

Av. wt. of 1,000 cc. seed	687.2 g.
Seed weighed with cakes 1 and 2	517.8 g.
Seed displaced by cakes 1 and 2	169.4 g.
1 gram seed = 1,000 cc.	1.455 cc.
169.4 g. seed $\times$ 1.455	246.5 cc.
Wt. cakes 1 and 2	82.2 g.
246.5	3.0
82.2	

Av. specific volume of cakes 1 and 2 is 3.

The cakes were weighed and measured two at a time, constituting a group, and thus the average specific volume for that group were obtained. All groups for a baking were then averaged together in one figure and this alone is given.

The mix in Series I consists of sugar, butter compound, eggs, milk, flour and lemon extract, all measured or weighed by the baker as usual, except that he took particular pains to do everything as accurately and as uniformly as possible. Two ounces of Cleveland's baking powder went into each batch of five dozen cup cakes, which were baked in five tins, holding twelve cakes each. The first batch was baked by the time the second batch was ready, and the second was baked in the same place in the oven as the first, the bakers striving for uniformity throughout. In these large ovens the temperature changes very slowly, the oven baking uniformly for hours at a time.

The two batches were thus contained in ten tins of a dozen each, and the cakes selected for measurement were taken from each pan in an arbitrary manner, so as to avoid any conscious selection. About 30 per cent of the cakes baked were measured.

TABLE I—AVERAGE SPECIFIC VOLUME OF CUP CAKES—SERIES I

Baking No.	No. of cakes averaged	With egg albumin % albumin in parentheses	Without egg albumin
1	12	2.99	3.03
2	6	2.99	2.99
3	17	3.22 (0.5)	3.10—Batch A
4	17	3.21 (2.0)	3.10—Batch B
5	18	2.99 (0.5)	3.00
6	18	3.10 (1.0)	3.13
7	18	3.21 (2.0)	3.17
8	20	2.99 (5.0)	3.06
9	20	3.20 (20.0)	3.18
Average (Weighted mean)		3.097	3.108
		3.10	3.11

The 94 cup cakes made with albuminized powder have an av. sp. vol. of 3.10; 146 cup cakes made with non-albuminized powder have an av. sp. vol. of 3.11. This advantage in favor of non-albuminized powder is scarcely significant in view of the following facts: In Baking 3, two batches designated A and B were baked, neither of which contained egg albumin in the powder used. This was to ascertain what variation might occur when the two batches were identical in every way, although the bakers thought that different powders were being used.

Batch A averaged 3.22 for 17 cakes.

Batch B averaged 3.10 for 17 cakes.

This is a variation of 0.12 in 3.22 and the largest in any one baking. 2.99 was the minimum sp. vol. and occurs three times, twice with egg albumin and once without; 3.22 is the maximum and occurs in the series without the albumin; 3.21 and 3.20 occur with albumin. If the first three bakings are excluded

from the average because only the last five were baked, both with and without albumin, the average for those without egg albumin is still 3.11. Egg albumin was twice in the second batch baked, three times in the first baked.

Bakings 1 and 2 were bought over the counter, before the firm knew they were to be tested. They serve as controls as do the two batches in Baking 3.

#### JUDGMENTS—SERIES I

Bakings 3 and 4 were lost.

Baking 5—In breaking three cakes of each batch, the texture of cakes A (without egg albumin) was a little, though a very little, better than B (with 1 per cent added albumin).

Baking 6—B. cakes (without egg) judged the better mix. B. cakes thought to be slightly larger in volume. (This was not the case when measured.)

Baking 7—B. cakes (without egg) a shade lighter in color than A. cakes. No other differences noticed between A and B cakes.

Baking 8—Judgment lost.

After studying the two batches in every way possible, the final conclusion of the two bakers was about as follows: "Well, it's pretty hard to say which is the better; they are just about as nearly alike as they could be."

As to the variables entering into the work, the average weight of 1,000 cc. of rape seed was determined for each baking and these averages had a maximum variation of 1.7 per cent. This is the smallest variable. The weights of cakes varied greatly. Commonly this was 10 to 15 per cent between the heaviest two and the lightest two in any bake. The weight of rape seed displaced by cakes varied in about the same manner and indicated that no large or constant error of measurement entered into the series. These variations are best shown in Table II.

TABLE II

Number of baking		% difference between max. and min. weights of cakes	Number of baking		% difference between max. and min. weights of cakes
1	10	14	6 A	1	7
2	2	12 (6)	B	17	8
3 A	13	12	7 A	28	23
B	14	17	B	11	9
4 A	10	13	8 A	13	13
B	15	13	B	13	15
5 A	15	17			
B	17	15	AVERAGE	12.6	13.4

The most striking difference between Columns 2 and 3, in the same baking, is in the second baking. In the original data there is one weight of "Rape seed displaced by cakes," that looks quite suspicious. Casting out this weight, the final average in this baking is changed from 2.99 to 2.96 and the "percentage difference" to 6. Introducing the figure 2.96 into the final results changes the grand average for cakes without albumin from 3.1084 to 3.1072. In other words, it does not change the final average at all, for, when reported to the correct number of places, we still have 3.11.

This discussion of the errors gives an idea of their magnitude and also shows that the number of measurements has been large enough to make even that value which is most probably in error, without effect on the final average.



## CONCLUSION—SERIES I

The addition of egg albumin to the baking powder used in baking cup cakes was entirely without any measurable result, and without any observable effect that could be seen by two experienced bakers.

## SERIES II

In the second series, another bakery did the work, biscuits were used, and temperatures and times of baking recorded. All biscuits in this series contained:

Flour.....	2 lbs
Baking powder.....	2 oz.
Compound (melted).....	3 level tablespoonsful
Salt.....	1 level tablespoonful
Milk.....	$\frac{3}{4}$ quart

The compound was added last. The poorest flour of which the baker knew was used in the first three bakings, because it has been claimed that an albuminized powder shows to greatest advantage with very weak flour. In the fourth baking a strong flour was used. The baker controlled everything in this series except the baking powder which was K. C. Baking Powder. The two ounces were weighed to a tenth of a gram and then to one portion was added the per cent of egg albumin shown in brackets in Table III. The albumin was mixed into the powder by rolling two hundred times on a rubber sheet in the manner used by assayers in mixing powdered ores. The non-albuminized powder was rolled to the same extent, to expose it to the air in like manner. The dough was rolled out between thin strips of wood upon which the rolling pin rested, to secure an even thickness of dough before the biscuits were cut out. Dough left from the first cutting was discarded.

The first batch was baked while the second was being prepared, the second then went into the same place in the oven that the first had occupied. Twice the egg albumin was in the first or A batch, twice in the second or B batch. Four biscuits were usually weighed and measured at the same time, giving a specific volume for the group, and the specific volumes for the groups were averaged together (weighted if less than four in a group) to give the av. sp. vol. for that baking. Table III shows the results:

TABLE III—AVERAGE SPECIFIC VOLUME OF BISCUITS—SERIES II

Baking No.	No. biscuits in average	Time baked in Minutes	Temp. of baking ° F.	Average sp. vol. of egg albumin in brackets
1 A.....	29	11	498	500
B.....	31	13	500	3
2 A.....	24	11	494	5
B.....	21	11	495	8
3 A.....	13	12	485	7
B.....	13	12	487	2
4 A.....	17	12	489	90
B.....	19	12	490	7
Average (weighted mean) { of 85 biscuits with egg albumin.....				2.548
{ of 82 biscuits without egg albumin.....				2.550

Bakings 2, 3 and 4 set in the pans ten minutes before going into the oven, as certain companies making an albuminized powder claim this to be advantageous. Retaining three places in the final result, the non-albuminized powder gave biscuits with the same sp. vol. as the albuminized powder, namely, 2.55. The lightest biscuits (2.78) were without egg, the next lightest (2.67) with 0.2 per cent egg, the next lightest (2.64) with 0.1 per cent egg, the next lightest

(2.62) without egg. The lightest biscuit was baked two minutes longer than it should have been.

## JUDGMENTS—SERIES II

Baking 1—Batch B slightly better than A (0.1 per cent) but very hard to decide.

Baking 2—Batch B is a little better than A (0.2 per cent) but both very nearly alike.

[Assistant Baker: A (0.2 per cent) biscuits a little better than B.]

Baking 3—Batch A slightly lighter by texture. B (0.5 per cent) raised a little higher (external appearance).

Baking 4—Batch B (1.0 per cent) quite a bit better than A.

These results are rather indecisive, for only in the fourth baking was any decided advantage recorded by the baker's judgment.

In Baking 2, the head baker and his assistant differed, thus showing no real difference between the two batches.

In Baking 3, Batch B was allowed to stand 13½ minutes, before going into oven, instead of 10, as for A, through a mistake in watching the time.

It was intended to continue this series, but work had to be stopped on account of other duties.

## SERIES III

The third bakery (Imperial Bakery) did the baking and controlled all factors except baking powder, shortening and salt, which were weighed to a tenth of a gram and supplied to the baker at time of mixing. A weak flour was used throughout.

Mix used:

Flour.....	3 lbs.
Baking powder.....	3 oz.
Cottolene (cold).....	3 oz.
Salt.....	$\frac{1}{2}$ oz.
Milk.....	1 qt.

The flour, baking powder and salt were first mixed by hand, then the cottolene worked in by hand, and last the milk added. The baking powders used were Crescent, manufactured with egg albumin and designated C; K. C. powder, manufactured without egg; Atlas, manufactured without egg and designated A; Giant, manufactured without egg and designated G; Interstate, manufactured without egg and designated I. All these powders are alum phosphate powders. Egg albumin was added to part of the non-egg powders in certain bakings in the same manner as in Series II. Bakings 4, 5 and 6 were divided into two portions, designated 1st and 2nd half. The 1st half was rolled out and baked about 9 A.M. The 2nd half stood in the proof closet until about 2 P.M. and was then rolled out and baked. This was to test the claim that dough made with albuminized powder could stand several hours, or over night, and still make good biscuits. The baker could not arrange any other time for the two bakings than 8.30 A.M. and 2.00 P.M. The order of baking batches was that given in Table III. All dough was rolled to a uniform thickness between narrow strips of wood, and that left from the first cutting was discarded.

The difference of 34 in 2627 is 1.3 per cent, and is in favor of biscuits baked with albuminized powder. The greatest gains for powder with albumin are found in the early part of Series III, when one brand of

powder, albuminized as it comes on the market, is directly compared with a non-egg powder as manufactured. This is really unfair, as the two powders used may differ in their effects, aside from the egg albumin in one of them. The most striking failure of egg albumin to improve a given powder is shown

TABLE IV—AVERAGE SPECIFIC VOLUME OF BISCUITS—SERIES III

Baking No.	No. averaged	Time baked Min.	Temp. baking ° F.	Av. Kind of sp. vol. bk. pdr.	Per cent egg alb.
1 A.....	31	10	495	2.79 C.	0.17
B.....	28	10	495	2.54 K. C.	0.0
2 A.....	28	10	470-1	2.60 K. C.	0.0
B.....	28	11	471-4	2.75 C.	0.17
3 A.....	28	10	465	2.71 A.	0.0
B.....	32	10	465	2.63 C.	0.17
C.....	32	10	465	2.53 G.	0.0
4 C 1st half.....	18	10	450-5	2.66 G.	0.0
B 1st half.....	18	10	455-60	2.63 C.	0.17
A 1st half.....	17	10	460	2.70 A.	0.0
5 C 2nd half.....	14	10	458-60	1.08 G.	0.0
B 2nd half.....	14	10	458-60	2.20 C.	0.17
A 2nd half.....	13	10	458 60	2.15 A.	0.0
5 A 1st half.....	20	12	430-5	2.96 I.	0.0
B 1st half.....	20	12	430-5	2.96 I.	0.2
C 1st half.....	20	12	430-5	2.90 I.	0.5
5 A 2nd half.....	18	12	443-5	2.56 I.	0.0
B 2nd half.....	18	12	443-5	2.54 I.	0.2
C 2nd half.....	18	12	443-5	2.57 I.	0.5
6 A 1st half.....	20	10	455	2.65 G.	0.0
B 1st half.....	20	10	455	2.65 G.	0.2
C 1st half.....	20	10	455	2.59 G.	1.0
6 A 2nd half.....	16	10	460	2.27 G.	0.0
B 2nd half.....	16	10	460	2.25 G.	0.2
C 2nd half.....	16	10	460	2.26 G.	1.0

Average (weighted mean) of 271 biscuits with egg..... 2.627 2.63

Average (weighted mean) of 238 biscuits without egg..... 2.593 2.59

Difference..... 0.034

in Bakings 5 and 6, where the same powder was used first without egg, second with 0.2 per cent added egg, and third 0.5 per cent added egg in Baking 5. In the first half, which was baked at once, the sp. vol. fell from 2.96 with no egg and with 0.2 per cent egg, to 2.90 with 0.5 per cent egg. In Baking 6, 0.0 per cent, 0.2 per cent, and 1.0 per cent egg were present in a second can of Giant powder. The sp. vol. fell from 2.65 with no egg, and 0.2 per cent to 2.59 with 1.0 per cent egg, and in both Bakings 5 and 6, these figures are the averages of 20 biscuits.

SUMMARY OF RESULTS OF BAKING TESTS ON BISCUITS—SERIES III

Baking No.	Temp. baking	Batch	Bk. pdr.	% alb.	REMARKS
(1).....	495	B	K. C.	0.0	Better in looks, taste, odor (Judgment of four persons)
(2).....	470-74	B	C.	0.17	Looks better than A. (K. C. 0.00%) no difference in smell or taste
(3).....	465	C	G.	0.0	Best
		B	C.	0.17	2nd
(4) 1st half.....	450-60	A	A.	0.0	Poorest
		A	G.	0.0	Best
		B	C.	0.17	2nd
(4) 2nd half.....	458-60	A	A.	0.0	Poorest
		B	C.	0.17	Best
		C	G.	0.0	2nd
(5) 1st half.....	430-35	C	I.	0.5	Very poor
		B	I.	0.2	2nd
		A	I.	0.0	Very poor
(5) 2nd half.....	443-45	C	I.	0.5	Best
		B	I.	0.2	Poorest
		A	I.	0.0	2nd
(6) 1st half.....	455	C	G.	1.0	Best
		B	G.	0.2	2nd
		A	G.	0.0	Not bad
(6) 2nd half.....	460	C	G.	1.0	Best
		B	G.	0.2	2nd
		A	G.	0.0	Poorest

## JUDGMENT

When biscuits are judged by looks much greater differences are noted than by measurement. It appears that a fine looking, large biscuit may have no greater sp. vol. than a smaller and poorer looking biscuit. This is due to the fact that the larger biscuit is heavier, and the sp. vol. works out about the

same as for smaller biscuits. Just why this is so has not been determined.

This difference in judging by looks and measurement is strikingly shown in Baking 1, when batch B (0.0 per cent) was given the preference in looks, taste and odor, by four bakers, separately, although A (C. 0.17 per cent) proved to be larger in sp. vol. by 0.25 in 2.79.

In Bakings 4, 5 and 6 the bakers awarded the honors very uniformly to the biscuits baked with albuminized powder. The differences were so marked that anyone could not fail to see them, yet, these differences do not show in the sp. vol. These were all baked at too low a temperature, and the 2nd half of a bake was always carried out after the dough had stood about five hours.

## CONCLUSION

It is the opinion of the writer that when bakings are carried out under normal conditions his work has not demonstrated the usefulness of egg albumin in baking powder, and especially in the very small quantity usually present, *i. e.*, from 0.1 to 0.2 of one per cent.

When the temperature of the oven is too low for baking biscuits properly, egg albumin seems to aid in producing a better biscuit.

When the dough is allowed to stand several hours before baking, a much better biscuit is produced by the powder to which egg albumin has been added.

OFFICE OF THE STATE CHEMIST  
BOISE, IDAHO

## IRON IN TOMATOES

By C. A. BRAUTLECHT AND G. CRAWFORD

Received September 5, 1914

Tomatoes have become of much importance as a garden vegetable during the last decade and present evidence indicates that they will become of greater importance. From the view-point of the food, physiological and agricultural chemist more knowledge of their chemical composition is therefore desirable.

Tomatoes are used as a food in many ways. While fresh, they are eaten raw or cooked; tremendous quantities are canned; they form the basis of many soups; large quantities of tomatoes, or their products, are used as sauces for meat or fish foods; in desert regions, or where good drinking water is scarce, canned tomatoes are used largely because of the water and vegetable acid they contain.

Considering the exchange in soil elements, there seems to be a general agreement that the tomato plant uses relatively little phosphoric acid, but more potash and nitrogen. Much of the potash remains in the vines and roots. In comparison with the amount of crop produced, the tomato does not remove much plant food from the soil.

The acidity of the tomato is supposed to be due to citric acid. A small amount of an alkaloid is also supposed to be present in the juice and this decreases as the fruit ripens. During ripening there is a progressive increase in the organic acids, sugars, starch and non-

protein nitrogen and a decrease in protein nitrogen and cellulose. The proportion of other constituents remains practically unchanged. The amount of sucrose in fresh and dehydrated tomatoes differs, due probably, to inversion resulting from ferments and organic acids. About 0.5 per cent of ether extract is obtainable from the dry matter of the tomato, this amount being reduced, however, by previous alcohol extraction.

Passerini<sup>1</sup> states that the pulp of the tomato contains two coloring matters, a yellow amorphous and a red crystalline substance. These are insoluble in water, soluble in amyl alcohol and very soluble in ether. Both are decolorized by chlorine and bromine water, while hydrochloric acid has no action on them. The yellow substance is much more soluble in alcohol than the red. R. Willstätter and H. H. Echer<sup>2</sup> state that lycopin, the coloring matter of the tomato, differs in several respects from carotin.

E. H. Jenkins and W. E. Britton<sup>3</sup> reporting results on two varieties of tomatoes found no difference between them in water and potash content, percentage limits for water and potash on eight samples being respectively 93.41 to 94.81 and 0.287 to 0.356. H. Snyder<sup>4</sup> found no chemical difference between three varieties. He reports analytical results on three samples: Water, 93.6 to 93.9; protein, 0.80 to 0.86; carbohydrates, 3.79 to 3.85; and ash, 0.54 to 0.69 per cent. W. B. Alwood and W. Bowman<sup>5</sup> found in four samples of one variety: Water, 91.2 to 94.0 per cent; protein, 0.78 to 1.25; carbohydrates, 3.60 to 4.07; fat, 0.33 to 0.47; and ash, 0.34 to 0.73 per cent. W. O. Atwater and A. P. Bryant<sup>6</sup> report on analysis of two samples of canned tomatoes: Water, 94.0 and 94.3 per cent; protein, 0.9 and 1.2; carbohydrates, 3.9 and 4.0; fat, 0.2 and 0.4; and ash, 0.5 and 0.6 per cent. One sample of ash contained 5.8 per cent lime, 8.7 per cent phosphoric pentoxide, 68.1 per cent potash and 3.7 per cent magnesium oxide. A number of other investigators—Ricciardelli, A. F. Bacon and P. B. Dunbar, and Albanarg—report similar results of a few analyses of tomatoes.

It is our intention to report the quantity of water, ash and iron in eleven samples of Florida canned tomatoes from different parts of the state. In the literature available we have found no figures showing the amount of iron in tomatoes.

The tomatoes were cut up and canned without appreciable loss of pulp or juice. When received at the laboratory they were cut up in a meat chopper without loss of juice and the water was determined by loss on evaporation of 150 g. samples at 110° to constant weight. The residue or total solids was ashed in thick porcelain dishes in a muffle furnace, at the lowest possible temperature, yielding a fine gray, white or buff colored ash. This was weighed, pulverized and iron determined in duplicate samples of about 0.2 g. The ash was then digested in hydrochloric acid and

again in sulfuric acid. The solution, free from hydrochloric acid, was reduced with hydrogen sulfide, the excess of hydrogen sulfide removed, the solution cooled and the iron titrated with standard potassium permanganate solution.

PERCENTAGE OF WATER, ASH AND IRON IN FLORIDA TOMATOES  
Iron as Ferric Oxide

Sample No.	Location	County	Water	Ash	whole		
					ash	tomatoes	soil
1	Lake City,	Columbia	94.0	0.39	11.53	0.046	3.03
2	Ponce de Leon,	Holmes	93.0	0.58	4.38	0.026	3.29
3	Lake Park,	Suwanee	91.3	0.58	8.09	0.046	3.81
4	Dover,	Hillsboro	92.6	0.53	20.68	0.106	
5	Greensboro,	Gadsden	94.6	0.53	18.62	0.100	
6	Pensacola,	Escambia	94.6	0.55	22.25	0.123	
7	Paxton,	Walton	92.6	0.56	6.09	0.034	
8	Tallahassee,	Leon	95.0	0.49	7.75	0.037	
9	Summerfield,	Marion	95.3	0.38	21.45	0.083	
10	Green Cove Springs,	Clay	95.3	0.63	12.21	0.077	3.12
11	Tallahassee,	Leon	89.3	0.64	8.47	0.054	

Average..... 93.4 0.53 12.87 0.066 3.32

(a) Average of closely agreeing duplicates.

#### SUMMARY OF RESULTS

I—The tomatoes from ten counties in Florida contained from 89.3 to 95.3 per cent of water. Geographical location of plot on which the tomatoes were grown did not affect the water content. The average amount of water was 93.4 per cent.

II—The ash varied from 0.38 to 0.64 per cent, averaging 0.53 per cent. There was no fixed ratio between the water and ash or iron and ash.

III—The iron in the ash varied greatly from 1.53 to 7.78, average 4.50 per cent. Calculated to ferric oxide this would represent 4.38, 22.25 and 12.87 per cent, respectively. Iron was present in about the same amount in widely separated counties.

IV—Iron in tomatoes, calculated from the iron in the ash, ranged from 0.012 to 0.037 per cent, averaging 0.023 per cent. Calculated to ferric oxide, this would represent 0.034, 0.123 and 0.066 per cent, respectively.

V—In soil on which these tomatoes were grown (four samples), there was from 1.06 to 1.3 per cent iron, equivalent to 3.03 and 3.72, or an average of 3.32 per cent ferric oxide.

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#### BLOOD-CHARCOAL AS A PURIFYING AGENT FOR ARSENIC SOLUTIONS PREVIOUS TO TITRATION<sup>1</sup>

By ROBERT M. CHAPIN

Received September 3, 1914

Whenever possible, arsenic is estimated by the highly accurate and convenient method of titration with iodine. As necessary conditions, the solution must be free from other substances capable of absorbing iodine during the titration and from coloring matter to obscure the end points.

This laboratory has been required to examine very many samples of the arsenical dipping baths<sup>2</sup> now so largely used for ridding cattle of Texas-fever ticks. The important insecticidal ingredient of these baths is an alkaline arsenite, and it is in this form that the arsenic is introduced when the baths are prepared.

<sup>1</sup> Published by permission of the Secretary of Agriculture.

<sup>2</sup> Compare *Farmers' Bulletin* 603, U. S. Dept. of Agric.

<sup>1</sup> *Stag. Sper. Agrar.*, 18, 545.

<sup>2</sup> *Ztschr. physiol. Chem.*, 64, 47.

<sup>3</sup> *Conn. Agr. Expt. Sta. Ann. Rpt.*, 1895.

<sup>4</sup> *Minn. State Bull.*, 63.

<sup>5</sup> *Va. State Expt. Sta., Bull.* 4.

<sup>6</sup> *U. S. Dept. Agr., Bull.* 28.



But with accumulation of dirt and excrement from the cattle during months of use in dipping vats, the baths become culture media for microorganisms which may either oxidize the arsenic, or reduce it again, depending upon prevalent conditions.<sup>1</sup> In a sample of used bath, therefore, it is necessary to determine both actual arsenious oxide and total arsenic.

The organic matter present in used arsenical dipping baths interferes with titration by iodine in both the undesirable ways; it absorbs iodine under the conditions of the titration, thus rendering the end points inaccurate and fugitive, and it imparts color to the solution. An obvious first step is to acidify and filter the bath, adding also a clarifying agent. Purified kaolin or kieselguhr are only moderately beneficial, but in blood-charcoal was found an agent which, used in small amount and with brief digestion, produced water-white filtrates wherein the end points with iodine came out sharply and permanently. Before the substance could be employed in routine analytical work, it was necessary to ascertain if its well-known adsorptive and oxidative powers<sup>2</sup> would affect the arsenic present.

The simple plan of investigation involved treatment of measured portions of a standard arsenious acid in parallel, with and without charcoal, followed by titration with standard iodine. Approximately twentieth-normal solutions were employed and to each 25 cc. of arsenious acid solution was added 5 cc. of 10 per cent (by weight) sulfuric acid, and 0.25 g. blood-charcoal (if any used), previous experiments having shown this quantity to be ample for the purification of 25 cc. of very filthy dipping baths. All filtrations followed by washing were carried to a total volume of 125 cc. Arsenious oxide was titrated in presence of sodium bicarbonate. For total arsenic the 125 cc. of filtrate and washings were boiled down to 50 cc. after addition of 3.5 cc. concentrated sulfuric acid and 2 g. potassium iodide. From the cooled solution, diluted to 250 cc., excess iodine was cautiously removed in presence of starch by a dilute solution of sodium sulfite (0.5 per cent of anhydrous salt), then acid was neutralized with sodium carbonate and bicarbonate, and after further dilution the titration was completed in the usual way.

chased as "acid-washed," was exhaustively purified with hydrochloric acid to free it from iron, consequently there is no reason to believe that the evident oxidative properties it displayed can be attributed to anything else than oxygen of the air likewise adsorbed by it, the power of charcoal to adsorb gases being sufficiently well known.

Other similar experiments, which in view of their simplicity are not detailed, showed that: (1) the amount of arsenious acid oxidized is dependent upon the amount of charcoal used as well as upon the length of heating but not at all upon the concentration of arsenious acid (at any rate between 5 cc. and 25 cc. of twentieth-normal solution in an original volume of 30 cc.); (2) arsenic acid is likewise slightly adsorbed, and likewise quantitatively returned to thorough washing.

As to the practical application of the above observations, it is believed that they may be of considerable assistance in the estimation of both arsenious and arsenic acids in a variety of substances. As a test of the decolorizing power of the charcoal, two grams of a sample<sup>1</sup> of London purple were digested with 100 cc. dilute hydrochloric acid according to the method of the A. O. A. C.,<sup>2</sup> and were then treated for five minutes at 60 to 70° C. with 2 g. blood-charcoal, being stirred most of the time. To obtain the most trying conditions, the solution was then at once filtered with suction, washing continued to a total volume of 250 cc., and the filtrate finally made to 300 cc. A 50 cc. aliquot, which is the quantity officially prescribed for each estimation—corresponding to 0.333 g. charcoal—developed no trace of purple color when treated with excess of either sodium carbonate or bicarbonate.

If actual arsenious oxide is to be determined it is of course necessary to obtain a "correction for oxidation" on the sample of charcoal to be employed, under the precise set of conditions which will prevail in the analysis.

The writer has previously recommended<sup>3</sup> the use of blood-charcoal in the assay of arsenical dips, noting the necessity for a correction, but at that time had reason to believe—and so implied—that it was chiefly attributable to adsorption. The precise cause of the

No.	PROCEDURE	Cc. N 20 I per 25 cc. As <sub>2</sub> O <sub>3</sub> sol.		Apparent loss; cc. N/20 I
		Without charcoal	With charcoal	
1	Direct titration for actual As <sub>2</sub> O <sub>3</sub> .....	25.14		
2	50 cc. As <sub>2</sub> O <sub>3</sub> , 10 cc. H <sub>2</sub> SO <sub>4</sub> , 0.50 g. charcoal, made to 100 cc. in stoppered flask mixed, and filtered after 40 minutes, discarding first runnings. Titrated 50 cc. for actual As <sub>2</sub> O <sub>3</sub> .....	...	24.47	0.67
3	In a 100 cc. beaker, low form, 25 cc. As <sub>2</sub> O <sub>3</sub> , 5 cc. H <sub>2</sub> SO <sub>4</sub> , 0.25 g. charcoal; stirred cold 5 minutes, filtered (a), washed, and titrated for actual As <sub>2</sub> O <sub>3</sub> .....	...	24.97	0.17
4	Similar to No. 3 except heated 5 min. on steam bath. Titrated for actual As <sub>2</sub> O <sub>3</sub> .....	25.15	24.91	0.23
5	Similar to No. 4 except heated for 40 minutes with occasional stirring. Titrated for actual As <sub>2</sub> O <sub>3</sub> .....	25.15	24.74	0.40
6	Similar to No. 5 except titrated for total arsenic.....	25.14	25.13	Nil

(a) The tests without charcoal were not filtered but were made directly to the desired volume.

In the above table each figure for an iodine titration represents the average result from at least two closely agreeing and wholly independent tests.

From the results it is evident that blood-charcoal, though slightly adsorbing arsenious oxide from acid solution, quantitatively returns it to thorough washing, not, however, in its original state, but more or less oxidized to arsenic acid. The charcoal used, pur-

phenomenon was not of prime importance in a purely technical paper, but in the interests of scientific accuracy the matter has since received this special study.

BIOCHEMICAL DIVISION, BUREAU OF ANIMAL INDUSTRY  
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<sup>1</sup> Obtained through the courtesy of C. C. McDonnell, of the Bureau of Chemistry and stated to contain approximately 25 per cent of dyestuff.

<sup>2</sup> Bureau of Chemistry, *Bull.* 107, Revised.

<sup>3</sup> U. S. Dept. Agric., *Bull.* 76.

<sup>1</sup> Compare U. S. Dept. Agric., *Bull.* 76.

<sup>2</sup> Compare Rosenthaler & Türk, *Archiv. der Pharmacie*, 244 (1906), 517.

# THE STRENGTH OF NITRIC ACID, PERIOD OF EXTRACTION, AND IGNITION AS AFFECTING THE GRAVIMETRIC DETERMINATION OF PHOSPHORIC ACID IN SOILS

By O. L. BRAUER

Received September 1, 1914

The question of a good measure of the available phosphorus in soils has long confronted chemists. The earlier investigators thought that by taking a solution of approximately the same strength as the plant acids they ought to get a correct estimate of the available phosphoric acid. In Europe, Dyer's<sup>1</sup> method of 1 per cent citric acid was extensively used, while the American chemists used  $N/200$  HCl. Veitch<sup>2</sup> extracted soil first with water and then with citric acid. Maxwell<sup>3</sup> used 1 per cent aspartic acid. As was pointed out by Hall<sup>4</sup> other factors entered into the determination, giving discordant results. Dargast<sup>5</sup> had already shown that the amount of phosphoric acid varied very much with the solvent. For a given soil he got the following results, in percentages: Aqua regia, 0.108; ammonium oxalate, 0.056; ammonium citrate, 0.042; acetic acid, 0.018; saturated  $\text{CO}_2$ , 0.015; and distilled water, 0.012. Moreover, it was shown that a given method might show low  $\text{P}_2\text{O}_5$  in a soil which would still show a good crop yield. This led to the conclusion that a weak acid does not get all of the soluble phosphates. Wood<sup>6</sup> showed that strong  $\text{HNO}_3$  removed much more  $\text{P}_2\text{O}_5$  than the weaker acids; for example, strong  $\text{HNO}_3$  extracted from the soil 0.23 per cent; 1 per cent citric, 0.08 per cent; 1 per cent citric in excess of enough to neutralize the lime, 0.085 per cent  $\text{P}_2\text{O}_5$ . Other things being equal, the crop yield showed general agreement with the amount of  $\text{P}_2\text{O}_5$  determined by analysis, when the strong acids were used.

Still there is considerable diversity in the strengths of acids used for extraction. Passernini<sup>7</sup> used concentrated  $\text{HNO}_3$ , Williams<sup>8</sup> used HCl (sp. gr. 1.115), and Fraps<sup>9</sup> used  $N/5$  HCl. In 1880 Professor Karl Schmidt showed that the amount of  $\text{P}_2\text{O}_5$  extracted varied with the strength of HCl employed. With 10 per cent hot HCl he got 0.562; with 5 per cent cold HCl 0.09; with 1 per cent cold HCl 0.084, in a soil containing 1.97 per cent total  $\text{P}_2\text{O}_5$ . The first part of the present investigation is to determine the strength of  $\text{HNO}_3$  necessary to obtain all the soluble phosphoric acid, or that included by Hilgard under the term "reserve" material.

Not only in the case of strength of acid used in the extraction is there great diversity of practice among chemists, but also in the length of time used in extraction. Williams<sup>10</sup> used concentrated HCl at the temperature of boiling water for ten hours. Sigmon<sup>11</sup> rotated for one-half hour and allowed to stand for 16

hours, then rotated one half hour again. Pagnoult digested for two hours. The official method of the U. S. Dept. of Agriculture<sup>2</sup> is to add the  $\text{HNO}_3$  and evaporate to dryness. Passernini<sup>3</sup> boiled on the sand bath for 1 hour.

The second part of this investigation is to determine the minimum time for the extraction of the soluble phosphates. Fraps<sup>4</sup> found that ignition increased the phosphate soluble in  $N/5$  HCl in both soils and phosphate materials. Lipman,<sup>5</sup> however, found that ignition decreased the phosphoric acid in soils which are soluble in nitric acid.

The third part of this investigation includes a study of the effect of ignition on the amount of  $\text{P}_2\text{O}_5$  set free by extraction with  $\text{HNO}_3$ .

**SOILS USED**—The soil was powdered up and passed through a 0.5 mm. sieve, and thoroughly mixed. Three soils of quite different  $\text{P}_2\text{O}_5$  content were selected.

1—A very rich, black, fine, silty loam, rich in phosphoric acid and humus from Arroyo Grande, San Luis Obispo County, California.

2—A light, sandy loam, of fairly good humus and  $\text{P}_2\text{O}_5$  content, from Anaheim, Orange County, California.

3—Heavy black adobe soil, low in humus and phosphoric acid, from Porterville, California.

**METHOD**—Weigh out 3 g. of air-dry soil and extract with  $\text{HNO}_3$  on the steam bath. Filter and wash until washings give no acid reaction. Evaporate to dryness and heat residue at  $130^\circ\text{C}$ . for 2 hours. Extract with 20 cc.  $\text{HNO}_3$  (sp. gr. 1.2). Filter and wash with warm water until the washings give no test for  $\text{Ca}_3(\text{PO}_4)_2$ . Add  $\text{NH}_4\text{OH}$  until a precipitate remains and dissolve in a couple of drops of  $\text{HNO}_3$ . Warm and add ammonium molybdate and stand at  $50\text{--}60^\circ$  for 12 hours. Filter and wash with solution of  $\text{NH}_4\text{NO}_3$  in  $\text{HNO}_3$ . Dissolve in  $\text{NH}_4\text{OH}$  and slowly add magnesia mixture to slight excess and stand over night. Filter and wash free from chlorides with a solution of 1 vol.  $\text{NH}_4\text{OH}$ , 1 vol. alcohol and 3 vol.  $\text{H}_2\text{O}$ . Dry in air bath and carefully ignite to constant weight.

**STRENGTH OF NITRIC ACID**—Samples of No. 1 were extracted with 50 cc.  $\text{HNO}_3$  and the rest with 20 cc.

TABLE 1—STRENGTHS OF ACID VARIED  
Per cent  $\text{P}_2\text{O}_5$  found in soil

Strength of acid	No. 1	No. 2	No. 3
15 N.....	0.517	.....	0.067
8 N.....	0.518	.....	.....
4 N.....	0.501	0.177	0.065
2 N.....	0.517	0.187	0.074
N.....	0.516	0.154	0.059
N.....	0.488	0.155	None

$\text{HNO}_3$ . They were all heated for two days on the steam bath, with a watch glass over the soil cup to prevent evaporation of the liquid. The percentages given are computed to the air-dry basis and are averages of three checks on sample No. 1, and two in the other cases, which, with the exception of three instances, did not differ by more than 0.01 per cent.

From Table I it appears that 2N  $\text{HNO}_3$  will give

<sup>1</sup> Ann. Agron., 25, 554.

<sup>2</sup> Div. of Chem., Bull. 43, 387.

<sup>3</sup> Chem. Abs. [2], 1911, p. 535.

<sup>4</sup> Fraps, THIS JOURNAL, 6, 416.

<sup>5</sup> C. B. Lipman, *Ibid.*, 4, 663.

<sup>1</sup> Trans. Lond. Chem. Soc., 65 (1894), 115.

<sup>2</sup> J. Am. Chem. Soc., 21, 1090.

<sup>3</sup> *Ibid.*, 21, 415.

<sup>4</sup> Trans. J. Chem. Soc., 39, 205.

<sup>5</sup> Ann. Agron., 9, 470.

<sup>6</sup> J. Chem. Soc., 69, 291.

<sup>7</sup> J. Chem. Soc. Abs., 1911, p. 535.

<sup>8</sup> U. S. Dept. Agr., Bull. 43, 387.

<sup>9</sup> THIS JOURNAL, 6, 416.

<sup>10</sup> J. Am. Chem. Soc., 17, 925.

<sup>11</sup> *Ibid.*, 29, 929.

as much soluble phosphoric acid as any stronger solution. The normal acid shows a slight decrease in yield in the second and third soils, and the  $N/5$  acid shows a decrease in every case. This agrees with the experience of Wood in that a certain strength of acid is necessary to get all the  $P_2O_5$ . However, it is not necessary to use the concentrated acid as did Passernini. The stronger nitric acids indeed are objectionable because they introduce certain difficulties by bringing down larger quantities of iron and aluminum.

**PERIOD OF EXTRACTION**—In each case 20 cc. of normal acid were used, and the per cent of  $P_2O_5$  given is an average of two closely agreeing checks.

TABLE II—PERIOD OF EXTRACTION VARIED  
Per cent  $P_2O_5$  found in soil

Period of extraction	No. 1	No. 2	No. 3
1 hr. ....	0.499	0.166	0.053
2 hr. ....	0.513	0.173	0.054
4 hr. ....	0.501	0.166	0.068
8 hr. ....	0.517	0.154	0.059

In one hour practically all the soluble  $P_2O_5$  is obtained. Two hours would be a liberal allowance and sufficient for all cases. Passernini boiled for 1 hour, which is about enough, but Williams boiled on the water bath for 10 hours, which was much longer than necessary. Pagnoul digested for two hours, which was about the right length of time. Hilgard employed the two-day period for digestion with concentrated  $HNO_3$ .

**IGNITION**—Each sample was extracted for 2 hrs. with 20 cc.  $N HNO_3$ .

TABLE III—TIME OF IGNITION VARIED  
Per cent  $P_2O_5$  found in soil

Ignition at red heat	No. 1	No. 2	No. 3
0 .....	0.513	0.18	0.054
$1/2$ hr. ....	0.499	0.199	0.046
1 hr. ....	0.487	0.195	0.041

In these cases the effect of ignition would seem to be similar to that obtained by Lipman, *i. e.*, to decrease the amount of  $P_2O_5$  soluble in  $HNO_3$ . Sample No. 2 shows practically no change, but the other two show appreciable decreases in the amounts of  $P_2O_5$  extracted, as the period of ignition lengthens and as between ignition and no ignition.

#### SUMMARY

I—Acid weaker than  $1N$  to  $2N HNO_3$  will not extract all the soluble phosphoric acid from a soil.

II—It is needless to extract with the acid for a longer period than 2 hours on the steam bath.

III—Ignition decreases the  $HNO_3$  soluble phosphoric acid in the soils.

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### COMPARISON OF SILICATES AND CARBONATES AS SOURCES OF LIME AND MAGNESIA FOR PLANTS

By W. H. MACINTIRE AND L. G. WILLIS  
Received September 21, 1914

The amount of calcium carbonate in soils has long been considered a very important consideration in their chemical examination; but calcium silicate has not been accorded universal recognition as an important source of lime for growing plants. The same may be said of the corresponding forms of magnesium.

In determining soil carbonates by the present official method of the Association of Official Agricul-

tural Chemists, we find that practically every soil has an *apparent* occurrence of carbonates, but at the same time possessing, in most cases of humid soils, a *lime requirement* by the Veitch method.<sup>1</sup> These two conditions—presence of appreciable amounts of carbonates and lime requirements, which indicate need of carbonates—are diametrically opposite, and were a soil to contain carbonates under laboratory conditions it would have no lime requirement. It is hard to conceive of a soil having 0.27 per cent calcium carbonate and yet having a lime requirement of 3812 lbs. of  $CaCO_3$  per acre (3,500,000 lbs. of soil); however, such results were obtained by the A. O. A. C. method for  $CO_2$  and the Veitch lime requirement method, respectively, upon the loam soil of the farm at this Station. This is strongly indicative of erroneous results from either one or possibly both of the methods cited.

The work of Marr<sup>2</sup> and the results reported by the writers<sup>3</sup> have shown that some soils absolutely free of carbonates, through elimination by dilute acid digestion, will produce heavy evolution of  $CO_2$  from the action of boiling acid upon carbonaceous matter. Marr concluded from his work that the use of 1:50  $HCl$ , and boiling with greatly reduced pressure, gave correct results. Until recently, practically all of the methods advanced for the determination of soil carbonates were based upon the supposed necessity of boiling the soil with acid to completely decompose carbonates and to expel from solution the liberated  $CO_2$ . The more recent work of the writers<sup>3</sup> has demonstrated that phosphoric acid is less active than hydrochloric acid upon soil organic matter and that 1:15  $H_3PO_4$  will liberate and expel from solution all carbonate  $CO_2$  at room temperature with about a 4-inch vacuum. In recent unpublished work the writers are making determinations upon treatments of about 400,000 pounds of limestone per 2,000,000 lbs. of soil and the carbonates from this treatment are entirely liberated by 1:15  $H_3PO_4$  with suction and without heat.

The Association of Official Agricultural Chemists has recognized the incorrectness of its method and is now studying the two methods above cited.

It will thus be seen that in many cases all of the  $CO_2$  found by analyses of soils when boiling with acid has been erroneously considered as in combination with lime, while the lime has occurred largely in the form of silicates and not as carbonates.

#### CORRELATION BETWEEN ACIDITY AND ABSENCE OF CARBONATES

Gaither,<sup>4</sup> in a comprehensive study of a large number of Ohio soils, found that almost invariably there was a close correlation between acidity, as indicated by the litmus-paper test, and absence of carbonates by his modification of the Marr method. We should probably note, however, that the authors have found that soils rich in silicates of calcium and magnesium,

<sup>1</sup> Jour. Am. Chem. Soc., **34** (1902), 1120.

<sup>2</sup> Jour. Agr. Sci., Vol. III, Part 2, 155–160.

<sup>3</sup> Tenn. Sta. Bull., **100**.

<sup>4</sup> THIS JOURNAL, **5** (1913), 138.



but devoid of carbonates, will react alkaline toward litmus paper. The litmus-paper test, then, will show acidity in the absence of carbonates, except when there is a considerable amount of the alkali-earth silicates.

#### NATIVE OCCURRENCE OF SILICATES AND THEIR FORMATION IN SOILS

It has been the observation of the senior author that it is a rare exception to find in the Eastern States a cultivated soil which will react alkaline to litmus, unless it has been limed. It would seem, then, that the crops of many of our soils are *compelled* to secure much of their lime from the carbonate of lime formed by the hydrolysis of calcium silicate in carbonated water.

While the occurrence of native lime silicates has received but scant consideration, there has been even less attention paid to the formation of silicates from lime treatments. Total lime, determinations by one of the writers,<sup>1</sup> upon the lime-treated plots of the Pennsylvania Station has shown that the reaction between lime and silicates continues long after attaining alkaline conditions by the satisfying of the *immediate lime requirement*. It was shown that of the total increase of lime over the check plots as a result of the lime treatments, nearly 35 per cent was accumulated as silicates. Investigations recently reported from the Tennessee Station<sup>1</sup> have shown that amounts of  $\text{CaO}$ ,  $\text{Ca}(\text{OH})_2$  and precipitated  $\text{CaCO}_3$ , in excess of requirements of acidity, have very quickly united with soil silicates. It was found that the burnt and hydrated forms, in amounts equivalent to lime requirements, acted directly with silicates and without carbonation, as in the Veitch procedure, when the treatments were mixed throughout the soil. The precipitated carbonate seemed to combine with siliceous materials as quickly as the oxide and hydrate. The same experiments have shown decidedly quicker reaction between siliceous soil compounds and the oxide, hydrate and precipitated carbonate than between silicates and ground limestone, in excessive amounts of equal basicity. It was also shown that though lime reacts extensively with siliceous materials the silicates formed function in the same manner as does the carbonate but to a lesser degree, which means that *there is conservation of lime in soils when it is present as silicate*.

#### BENEFICIAL EFFECTS OF CALCIUM SILICATE

In extensive plot work at the Tennessee Station marked effects are noticeable from liming over a nine-year period, during which nine crops of cow-peas and nine of wheat have been grown, though only 1800 lbs. per acre of lime were applied—an amount just sufficient to neutralize the acidity requirements indicated by the Veitch method. It is very probable that the present favorable results from liming nine years ago are due to residues of lime in the form of calcium silicate and not to calcium carbonate.

It has probably not been sufficiently emphasized, if emphasized at all, that the average amounts of lime applied are required to neutralize "acidity" or to

satisfy lime requirement; and that the lime of caustic or carbonate formed shortly combines with acid silicates, preventing any accumulation of carbonates as the result of treatments. Gardner and Brown<sup>1</sup> found that applications of burnt lime and ground limestone, in amounts indicated by the Veitch method, reduced the average requirements of a large number of plots by 71 and 72 per cent, respectively. The analyses for residual lime requirements were made about eight months after treatments. This strongly indicates that the continued beneficial effects of moderate liming must necessarily have come from the carbonate of lime, which is derived from the silicates by action of carbonated water.

#### LITERATURE

Although the literature upon the beneficial effects of  $\text{CaSiO}_3$ , *under such designation*, is exceedingly scant, a great many data, offered as showing the continued good effects from field treatments of moderate amounts of burnt or carbonated lime, have been attributed directly to the original oxide or carbonate, whereas the beneficial results have been due indirectly to the original treatment, and directly to the continuation of the lime as silicate in the soil. Mieth<sup>2</sup> advanced the query, "Can the lime of calcium silicate serve as plant food?" and he studied the question by water-culture experiments with oats. He concluded that the  $\text{CO}_2$  exuded by root activities served to produce carbonated water, which decomposed the calcium silicate and formed free silicic acid and calcium bicarbonate. He further concluded that the easily decomposable calcium silicate should receive consideration as a source of lime for growing plants. Gregorie<sup>3</sup> found, in water cultures of rye, that calcium zeolite "stimulated both root and aerial development," both of which were retarded by an excess of  $\text{CaCO}_3$ . Immendorf<sup>4</sup> regarded liming with lime containing soluble silica as beneficial in connection with the formation of zeolites. Pfeiffer,<sup>5</sup> in reviewing literature and discussing the work of Immendorf, concluded that the preponderance of evidence indicated beneficial effects from the use of siliceous lime. Von Feilitzen<sup>6</sup> secured better results with the finest lime, which reacts most extensively with silicates as shown by results published by this Station.<sup>7</sup>

#### SILICATES AS SOURCES OF CARBONATES IN SOIL SOLUTIONS

The data presented in Table I show the comparative amounts of lime and magnesia conveyable in solution as bicarbonates to plants, from carbonates and silicates as the sources of the bases.

These results were secured by placing each charge, in the amounts designated, in 500 cc. of distilled water in glass cylinders and passing a current of  $\text{CO}_2$  through the water for 4 hours continuously. The  $\text{CO}_2$  entered at the bottom of the cylinders and at such a rate as to

<sup>1</sup> Pa. Sta. Annual Report, 1910-11, 76.

<sup>2</sup> Landw. Vers. Sta., 74 (1910), No. 1, 81; No. 2, 120.

<sup>3</sup> Exp. Sta. Rev., 23, 527.

<sup>4</sup> Ibid., 26, 34.

<sup>5</sup> Ibid., 29, 520, and 30, 127.

<sup>6</sup> Ibid., 23, 426.

<sup>7</sup> Loc. cit.

<sup>1</sup> Tenn. Bull., 107.

keep the substances in suspension. At the end of the 4-hour period, the suspended matter was quickly removed by filtration through Buchner filters with suction and the solutions titrated with  $N/20$  acid, methyl orange being used as an indicator. It will be noted that

TABLE I—COMPARISONS OF SOLUBILITIES OF FINELY GROUND MINERAL CARBONATES AND SILICATES OF CALCIUM AND MAGNESIUM IN CARBONATED WATER—PERIOD OF CONTACT, 4 HOURS

SUBSTANCE	Cc. $N/10$ acid to neutralize	Alkalinity in filtrate of g. $CaCO_3$ carbonated per liter	G. $SiO_2$ per l. $H_2O$
Wollastonite ( $CaSiO_3$ )—10 g. ....	54.2	0.542	0.0566
Limestone ( $CaCO_3$ )—10 g. ....	90.0	0.900	
Serpentine ( $MgSiO_3$ )—10 g. ....	21.6	0.216	0.0162
Magnesite ( $MgCO_3$ )—10 g. ....	28.0	0.280	
Wollastonite and serpentine—10 g. each.	69.35	0.6935	0.0840
Precipitated chalk ( $CaCO_3$ )—10 g. ....	117.3	1.173	0.0020
Pptd. chalk and serpentine—10 g. each.	121.2	1.212	0.0254
Wollastonite—20 g. ....	92.2	0.922	

the silica found in solution would account for but a small part of the  $CaO$  and the  $MgO$  as dissolved silicates, even assuming that the bases were combined as silicates with the  $SiO_2$  found, instead of its occurring as hydrate  $SiO_2$ . The same has been found to be true of the drainage waters from soils devoid of carbonates.

#### PLAN OF EXPERIMENTS WITH CALCIUM AND MAGNESIUM SILICATES

These observations, together with the fact that not only silicates but pure  $SiO_2$  will decompose calcium and magnesium carbonates and that the affinity of  $MgO$  for  $SiO_2$  and  $TiO_2$  is so great as to prevent the occurrence of magnesium carbonate as a solid in soils,<sup>1</sup> suggested a comparison between the silicates of calcium and magnesium, and the carbonates of the two elements. The two soils used in the work were a silty loam of "rotten" limestone origin and a sandy clay loam. Both soils were low in total lime and devoid of carbonates; and each had a lime requirement of about 1 ton of calcium carbonate per 3,500,000 lbs. of soil. The sandy loam contains a considerable quantity of red clay and was apparently benefited physically to a much greater extent than the silty soil, which had a decided tendency to bake. In other basket work upon the same soils the Veitch method had been used as a basis of  $CaO$  and  $MgO$  treatments without cropping. In one set of treatments in this previous work,  $CaO$  and  $MgO$  were applied separately, in amounts chemically equivalent to 16070 lbs. of  $CaCO_3$  per 3,500,000 lbs. of soil in excess of the indication of the Veitch method, both  $CaO$  and  $MgO$  being supplied as c. p. precipitated carbonates. It was found, however, that prior to the seeding of clover, the  $MgCO_3$  had been entirely decomposed with dissipation of the  $CO_2$ , hence the treatments in the magnesium carbonate pots were equivalent to finely divided magnesium silicate. In the silicate treatments the  $CaO$  and  $MgO$  treatments were duplicated as to amounts of  $CaO$  and  $MgO$ , but analyzed 100 mesh native mineral silicates, wollastonite and serpentine, were used as sources of calcium and magnesium. The treatments were thoroughly mixed throughout the entire soil mass. Eight-inch clay pots, painted inside and out with black asphaltum paint, were used as containers, two pots being used for each treatment and as a check on each

soil. No treatments other than lime and magnesium were given. Red clover was used as a measure of plant growth. The seeding was made in the middle of April and the pots were exposed, but protected from unfavorable weather. Distilled water was supplied almost daily.

#### GROWTH OF CLOVER RESULTING FROM TREATMENTS

From repeated seedings upon the two soils, we were unable to obtain any growth in the check pots.

The comparison between the crops of treatments A, Table II, and those of F is very striking for both soils. It should be emphasized that the amount of  $MgO$  applied

TABLE II—TREATMENTS

Each substance (or mixture) listed below was added in the amount equivalent to 16070 lbs. per acre in excess of the Veitch method indication.

A— $MgSiO_3$	D— $CaSiO_3$
B— $MgSiO_3$ and $CaSiO_3$	E— $CaCO_3$
C— $MgSiO_3$ and $CaCO_3$	F— $MgCO_3$

Checks received no treatment.

was the same in each case, and as before stated the magnesium carbonate had been entirely converted to silicates prior to seeding. Hence the treatments of A and F were identical in the amounts of  $MgO$ , but the magnesia was in one case (A) derived from 100-mesh serpentine, and in the other case (F) from silicates formed from precipitated magnesium carbonate.

In both soils the addition of each silicate alone gave decidedly increased yields. In one soil, the mixture of the two silicates increased the growth above that



A B C D E  
FIG. 1—RED CLOVER IN SANDY CLAY LOAM SOIL  
CHECK AND TREATMENT F—NO GROWTH

obtained from either silicate alone, while in the other soil the two-silicate treatments combined gave about the average of the growth secured from the two single silicate treatments.

In both soils the yields obtained from the silicates alone were decidedly better than the results secured from corresponding carbonates applied singly. The applications of the two silicates together were decidedly favorable in both soils, but the substitution of  $CaCO_3$  for  $CaSiO_3$  as supplementary to  $MgSiO_3$  proved decidedly disadvantageous. Experience from practice has, in a number of instances, shown unfavorable results from excessive liming, notably upon the heavily limed plots of the Pennsylvania Station.<sup>1</sup> Gardner and Brown<sup>2</sup> found, from pot work upon the above mentioned limed plots, that additional liming still further reduced the yield of clover. Densch,<sup>3</sup> in noting harmful effects of excessive liming, attributes

<sup>1</sup> Pa. Sta. Bull., 90.

<sup>2</sup> Loc. cit.

<sup>3</sup> Abs. Centbl. Bakt., 2 Abst., 39, (1913), No. 4, 159; 7, 160.

<sup>1</sup> Loc. cit.

the unfavorable results to reduction of nitrates to ammonia, and to the persistent occurrence of nitrites as well as to formation of nitro and nitroso compounds. Ritter<sup>1</sup> attributes injurious results of excessive liming on peaty soils to the poisonous oxidation products

The data indicate that  $\text{CaSiO}_3$  is decidedly superior to  $\text{CaCO}_3$ , both in its effect upon plant growth and as a form tending to conserve lime in soils.

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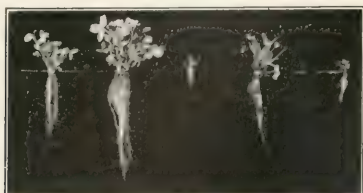


FIG. 11—RED CLOVER IN SILTY LOAM SOIL.  
CHECK AND TREATMENT F—NO GROWTH

of humus. It is evident from the results shown in Table III and Fig. 1 that while harmful results may be expected from excessive amounts of  $\text{CaO}$  as finely

TABLE III—GROWTH OF RED CLOVER, GRAMS AIR-DRY  
TOTAL OF 2 POTS FOR EACH TREATMENT OF EACH SOIL

	A	B	C	D	E	F
Treatment	Check	$\text{MgSiO}_3$ (serpentine)	$\text{MgSiO}_3$ and $\text{CaSiO}_3$	$\text{MgSiO}_3$ and $\text{CaCO}_3$	$\text{CaSiO}_3$ (wollastonite)	$\text{CaCO}_3$ (precipitated)
No. of plants	0	27	47	26	20	21
Wt. of plants	0	11.4813	12.2757	1.8889	13.8557	4.8917
ON SILTY LOAM						
No. of plants	0	14	30	30	9	0
Wt. of plants	0	1.3427	4.1743	0.1361	0.5892	0.0642
						0.0000

divided carbonates, the same may not be said of  $\text{CaO}$  in the silicate form.

#### SUMMARY AND CONCLUSIONS

Fallacious methods for the determination of carbonates have given data showing occurrences of soil carbonates in many cases where none existed.

The long continued effects of liming in small or moderate amounts is to be attributed not to a continuation of carbonates resulting from treatments, but to the conservation of lime as silicates.

Through hydrolysis, calcium silicate functions in the same manner as calcium carbonate, furnishing lime as bicarbonate to the soil solution.

Excepting phosphates, the occurrence of calcium in soils is very often almost entirely as silicates, while magnesia seldom exists as the carbonate, but is generally to be found as the silicate.

Magnesium silicate formed by  $\text{MgCO}_3$ , equivalent to 16070 lbs. of  $\text{CaCO}_3$ , per 3,500,000 lbs. of soil in excess of the Veitch method, was decidedly toxic, while the same amount of  $\text{MgO}$  applied as 100-mesh serpentine was very beneficial.

Calcium and magnesium mineral silicates, wollastonite and serpentine, were very beneficial when applied either singly or jointly.

Calcium silicate, in the quantities used, was decidedly superior to calcium carbonate, when the amounts of  $\text{CaO}$  were identical.

The addition of  $\text{CaCO}_3$  alone effected some increase, but it reduced the beneficial effects of serpentine when added thereto.

#### A SIMPLE METHOD FOR DETERMINING THE CRITICAL MOISTURE CONTENT OF SOILS

By R. O. E. DAVIS

Received September 14, 1914

#### SIGNIFICANCE OF THE CRITICAL MOISTURE CONTENT

The critical moisture content of a soil has been described by Cameron and Gallagher<sup>1</sup> as the moisture content at which the physical properties of the soil attain either a maximum or minimum value. This moisture content corresponds to that physical condition of the soil when it is most suited for cultivation and for plant growth. This condition is known to the practical greenhouse man as the optimum condition. It depends upon the moisture content, the aeration, the temperature, mechanical composition and structure of the soil, and the physical condition. The physical condition is the summation of the other factors, and since it is dependent on physical factors, the measurement of the factors has assisted in determining the best physical condition as the optimum condition for plant growth. The critical moisture content then has reference to the condition of the soil in regard to its physical properties and at the same time designates that condition of soil moisture suitable for the growth of plants. This means that the critical moisture content is the most important point to determine in the study of the physical condition of the soil. It is the only measurement that shows a definite correlation between the physical properties and the condition for the plant growth.

The importance of the critical moisture content has been pointed out by Cameron and Gallagher<sup>2</sup> and more recently by Free.<sup>3</sup> Free says, "It is a constant which means something. It may be determined in a dozen different ways and neither the condition of the determination, the history of the sample, nor the personality of the experimenter will affect its value. Unfortunately, it has one serious disadvantage—its determination is exceedingly tedious, laborious and costly."

The critical moisture content is the content at which the soil can be put in the best condition for plant growth, or it determines the best time for tillage operations. The plant can then best obtain the necessary water from the soil because all the other factors encouraging plant growth are at their best.

#### PREVIOUS METHODS OF DETERMINATION

The methods previously employed for obtaining the critical values of the soil were by the determination of the volume-moisture relation or the penetration-moisture relation. The penetration values, measured by the weight required to force a pointed instru-

<sup>1</sup> Bull. 80 (1908), Bureau of Soils, U. S. Dept. of Agric.

<sup>2</sup> Loc. cit.

<sup>3</sup> E. E. Free, "Studies in Soil Physics," *Plant World*, 14 (1912), 36.



ment a given distance into the soil, were determined at different moisture contents. When these values were plotted, using per cent of moisture and penetration as the coordinates, the resulting curve showed the minimum penetration values at the critical moisture content. In a similar way the critical moisture content may be determined by plotting the apparent specific gravity or the apparent specific volume at different water contents. All of these methods are exceedingly laborious requiring special apparatus and consuming much time. In addition, the penetration method is far from accurate, and the other methods are not all that could be desired in this respect.

A still further difficulty is that in securing uniform packing of the soil for the penetration or volume methods, the screening becomes increasingly difficult with increase in water content. With sandy soils this is not serious, but on soils of a silty or clayey character it may be very serious; in many cases screening is entirely impracticable, and in all cases it is accomplished with the expenditure of much patience and labor. The soil collects in little balls that will not pass through the screen, but with shaking become more compact and increase in size. These can be forced through the screen only by rubbing with the hand.

#### THE NEW METHOD

The method adopted as most simple after many experiments with various devices was that of following the capillary movement of water. In some experiments on capillary movement it was noted that after the removal of the soil column from water the movement of water took place for a time, and then ceased. This occurred even though the two layers of soil in contact with each other were very different in their water content. A soil comparatively wet would remain in contact with a soil that was dry for days without any appreciable change in the moisture relations. Experiments were carried out to determine, if possible, the relation of the water in the moist layer of soil to the critical moisture content.

Water, as it advances into a soil by capillary action, moves as a thin sheet covering the soil grains with a thin film of moisture. The thickness of this continuous film of water increases with the nearness of approach to the source of water supply. Between the source of supply and the advance film are all degrees of thickness of water film, from the condition in which the interstitial spaces are filled with free water to that in which the film is extremely thin. The critical moisture content is that in which the water is all in the form of films on the soil grains. Thus, when water is moving through a soil by capillary forces, the water content of the soil just where the water film has advanced farthest is the critical or optimum water content.

In practice it is not possible to measure the exact moisture content where the film is most advanced, but it is possible to break the capillary connection and allow a distribution of the soil moisture until the water is present mostly in the form of film moisture. The determination of the moisture in the first inch of the moist soil column has given values corresponding to

the critical moisture content as determined in the ordinary way.

The apparatus used was a tube of over an inch in diameter. Glass tubes were tried, but the most satisfactory ones were made of brass. Brass tubing, one and a half inches in diameter, was cut into one-foot lengths. The pieces were split lengthwise and in one of the halves was cut a slit half an inch wide extending to within one inch of each end. The slit was covered with a strip of celluloid held in place by drops of solder stuck to the inside of the tube. This affords a window through which the movement of water may be observed. To the edges of one-half of the brass tube at each end were soldered short pieces of copper wire. When the two halves of the tube were placed together the copper wires were bent over and held them together. By wrapping a rubber band around the tube, the halves may be held in position more firmly. The end that is placed in the water is closed by a piece of cotton cloth secured by a rubber band.

The advantages of this type of tube are several. The window affords a means of watching the course of the water as it advances in the soil column. However, the most important advantage is that the tube may be opened up and the soil column removed in its entirety. This can then be divided up and the moisture content of any section determined.

In making the determination of the critical moisture content the tube is filled with soil and one end placed in water. When the water has advanced several inches in the tube it is removed from the water and placed in a horizontal position until capillary movement practically stops. The tube is then opened and a moisture determination made of the moist column of soil in the inch at the extreme end to which the water has advanced.

Experiments to determine the value of this method for determining the critical moisture content of soils were made on seven samples of soils of varying character. They were: Cecil sandy loam, Volusia silt loam, Marshall clay loam, Arlington Farm garden clay, Colbert silty clay loam, Memphis silt loam and Lexington silt loam. The first four were used to obtain comparative results on packing, size of particle aggregates, and length of time necessary to obtain equilibrium in the soil column.

The results on the differences in packing are given in Table I.

TABLE I—EFFECT OF PACKING ON MOISTURE CONTENT  
PER CENT MOISTURE IN SOIL

PACKING OF SOIL	Volusia silt loam	Garden soil	Cecil sandy loam	Marshall silt loam
Loose.....	15.9	16.0	8.0	15.2
Moderate.....	16.2	16.5	8.5	16.1
Tight (air-free).....	16.8	17.3	8.7	17.3

This shows that the packing does exert an influence, but not so great as was at first expected. When more closely packed, the moisture content is somewhat higher than when loosely packed.

Table II shows the results of different size soil aggregates. The movement is irregular with the large aggregates and the amount of moisture is slightly less than with the smaller ones.

Table III demonstrates the influence of time on the moisture content. It may be seen that after removal from the water the tubes should be left for about 18 hours. Any movement of water after that length of time is very slight; in fact, is almost inappreciable. Leaving the tubes for a much longer time results in the loss of moisture by evaporation.

As a result of these experiments the method adopted was as follows: The air-dried soil is rubbed in a porcelain mortar just sufficiently to break up any lumps of soil. The soil is filled into the brass or glass tube closed at the lower end by cotton cloth. The end of

dry soil beyond the point to which the moisture has advanced is at least two inches.

The tube is opened and the moisture determined in

TABLE III EFFECT OF TIME ON MOISTURE CONTENT PER CENT MOISTURE IN SOIL

Time after taking out of water Hrs.	Cecil sandy loam	Marshall silt loam	Volusia silt loam
12	10.8	17.7	17.4
12	7.7	21.0	19.9
24	7.7	16.6	16.6
24	7.6	16.5	16.0
24	..	17.0	16.7
24	..	17.3	..
48	6.4	16.5	..
72	..	..	16.1

TABLE II EFFECT OF SIZE OF SOIL AGGREGATES ON MOISTURE CONTENT PER CENT MOISTURE IN SOIL

SIZE OF SOIL	Volusia silt loam	Garden soil	Cecil sandy loam	Marshall silt loam
Coarse ..	16.1	15.3	6.5	15.2
Fine ....	16.6	16.8	10.8	17.0

the tube is tapped on the table until the soil column becomes so solid that the top does not break when the tube is placed in a horizontal position. The tube is then placed in water until the soil column becomes wet an inch or more above the water level. The tube is then removed from the water, the wet end covered with a piece of sheet rubber to prevent evaporation, and placed

a sample taken from the first inch of moist soil next to the dry portion. This moisture content represents the critical moisture content of the soil.

Experiments made to determine the critical moisture content, as compared with that obtained from the moisture-apparent specific gravity curve, were made

TABLE IV—COMPARATIVE RESULTS ON SEVERAL SAMPLES OF SOIL

Soil	Per cent moisture by capillarity	Critical moisture content by apparent sp. gr.
Cecil sandy loam.....	8.7	8-9.0
Marshall silt loam.....	17.3	17-18
	17.0	
	16.5	
Garden soil.....	16.6	16-17
Volusia silt loam.....	16.7	16-17
	17.0	
Colbert silty loam.....	17.4	17-18
	17.0	
Memphis silt loam.....	14.5	14-15
	14.9	
Lexington silt loam.....	8.5	8-9
	8.7	

on several samples of soil. The curves of moisture-apparent specific gravity are shown in Figs. 1 and 2, and the results from the capillarity method are given in Table IV, which shows that there is a close agreement between the two methods.

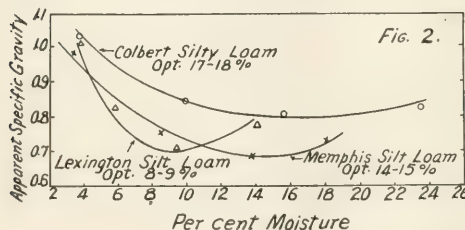
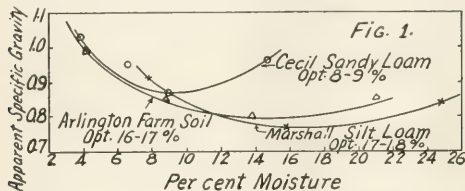
#### CONCLUSIONS

It is probable that the critical moisture content of a soil is its most important property in determining the physical condition of the soil.

Previous methods of determining the critical moisture content are tedious and laborious, requiring skill and special apparatus, and are only fairly accurate.

The capillary method of determining the critical moisture content is more accurate than the older methods, is simply and quickly carried out and requires little and inexpensive apparatus.

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in a horizontal position for about eighteen hours. The length of the soil column should be such that the

## LABORATORY AND PLANT

### A NEW AND IMPROVED FORM OF KJELDAHL DISTILLATION APPARATUS

By ARTHUR D. HOLMES<sup>1</sup>

Received August 8, 1914

There are so many forms of distillation apparatus for Kjeldahl determinations in use at present that a chemist contemplating making nitrogen determinations is immediately confronted with the problem of choosing that type which seems best suited to his needs. The factors to be considered primarily are simplicity

<sup>1</sup> Scientific assistant, nutrition investigations.

in design, low cost of construction, facility with which defective or broken parts may be replaced, durability, and ease and efficiency of operation. However, in spite of the fact that there may have been many types of apparatus devised, and many modifications of these types have been made, in almost any apparatus one or more of these essential features are omitted. Probably the most widely used apparatus for this purpose is one in which a metal tank containing several coiled block-tin tubes serves as a condenser. This has some serious disadvantages; one is, that if

the tank or any of the condenser tubes should leak, it becomes necessary to interrupt the use of the entire system while repairs are being made; another is that when it is desirable, at the end of the distilling process, to steam out the entire length of the condenser tube in order that none of the ammonia may be left in it, that can be done only when all the Kjeldahl flasks are ready for steaming at the same instant. In practice, however, the rate of distillation varies in the different flasks, and when a tank type of condenser is used one is obliged either to allow some of the flasks to distill until there is danger of bumping or else to steam out some of the others sooner than is desired. To avoid the difficulties involved in the use of this type of apparatus, which was formerly employed in this laboratory, the apparatus described hereafter (Fig. I), was designed, with the intention of incorporating to as great an extent as possible the features enumerated above. Since it has proven so satisfactory, and is so simple in construction that it may be made by the

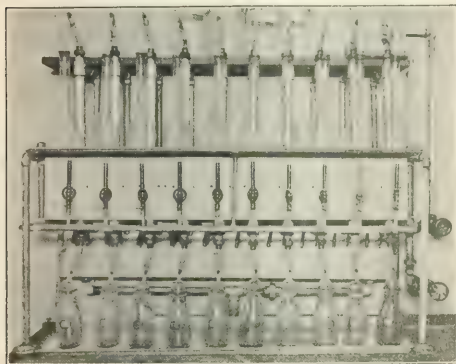


FIG I

average plumber, a detailed description should prove of value to anyone wishing to construct a similar distillation apparatus. The specifications and accompanying figures (which show details of construction of the complete apparatus set up in readiness for distillation) will convey a definite idea of its construction.

The bank of condensers, which may be composed of any desired number of units, is so constructed that each condenser is entirely separate in every way, even to having an individual water circuit, which may be regulated independently of the remainder of the system. As shown in Fig. II, each condenser jacket, A, is made of 1 1/4 in. galvanized iron pipe 18 in. in length, which terminate at each end, BB, in a 1 1/4 x 3/4 x 3/4 in. galvanized iron T. The inlet end of each condenser jacket is connected directly to the water supply pipe that is common to all by means of a 3/4 in. pipe, C, which carries a 3/4 in. brass union, D, and a "stop and waste" cock, E. The "stop and waste" cock is placed between the brass union and the water main, so that it is possible to shut off the water from any one of the condensers and remove it without interrupting the use of the other units of the system.

In Fig. III it will be noticed that a section of the supporting frame has been removed so as to show clearly the position and function of the "stop and waste" cock. It will also be noticed that the ends of water and gas pipes are fitted with plugs in order to prevent water and gas passing beyond the last condenser inlet and Bunsen burner, respectively. When the handle of the cock is in the position shown, the water circuit is shut off and the waste "pipe" is open, making it possible to drain the condenser jacket and to steam out the condenser tube from the distilling flask to the container in which the ammonia is caught and neutralized. To the outlet end of each condenser jacket is connected a 3/4 in. iron pipe, FF, that discharges into an overflow tank, G, which is common to the entire system.

The condenser tube HH, which is made of 3/4 in. block-tin type, may be easily removed, as it is slipped through the 3/4 in. brass union, II, on each end of the condenser jacket. Each brass union has a male thread on one end which is screwed directly into the T that forms each end of the condenser jacket. The other end of the union fits loosely over the block-tin pipe, and "lamp wicking," such as is commonly used for packing, is placed between the two portions of the unions, after which they are screwed tightly together, forming a water-tight joint. Thus, in case of injury the block-tin tubing may be removed by simply unscrewing the two parts of each brass union on the ends of the condenser.

The ordinary 500 cc. Kjeldahl flask J, used in connection with this apparatus, is connected by means of a rubber stopper, L, to the trap K, the tubing of which is bent at about a 30° angle and connected by means of rubber tubing, M, to the condenser tube. The modified adapter, O, used in connection with the apparatus, is connected by means of rubber tubing, P, to the lower end of the block-tin condenser tube and leads into an ordinary pint milk bottle, Q, which is used as a container for the acid into which the ammonia is distilled. The flasks are heated by Bunsen burners, R, screwed into a 1/2 in. piece of common iron pipe,

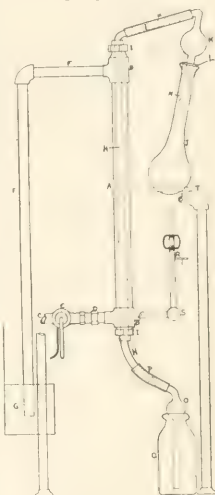


FIG II



FIG III



S, which is connected, as shown in Fig. 1, directly through a shut-off valve to the gas main. Gas may be admitted or shut off from the entire system by turning the main valve, or the individual burners may be regulated separately. The plate T, which supports the distilling flasks, is made of so-called "asbestos lumber," but this material was not found to be entirely satisfactory since it had a tendency to break after it had been used for a time. A more satisfactory support could have been made of sheet iron covered with a thick layer of ordinary asbestos board, since the asbestos would serve as a sort of shock absorber in the case of any bumping of the flasks. A piece of asbestos lumber is placed in front of and bolted to the condenser jackets in order to prevent heating of the water in the condenser by radiation of heat from the Bunsen burners.

The advantages of this type of distillation apparatus are:

1—Each condenser is entirely separate and may be removed as a whole, or in part, in case of injury, without interrupting the working of the remainder of the system. This is a decided advantage over the common type of condenser where a tank contains the spiral block-tin tubes of all the flasks in use, since, if one of the tubes or any portion of the tank leaked, it necessitated the dismantling of the whole system in order to make necessary repairs.

2—It is possible by means of the "stop and waste" cock not only to use any desired number of the units of the system, but also to regulate the flow of water through the different units.

3—The apparatus is simple in construction and made entirely of inexpensive materials such as a plumber would ordinarily have on hand.

The author wishes to express his appreciation to Mr. R. D. Milner for his interest and kind suggestions in connection with the construction of this apparatus.

LABORATORY OF NUTRITION INVESTIGATIONS  
OFFICE OF EXPERIMENT STATIONS

U. S. DEPARTMENT OF AGRICULTURE, WASHINGTON

### A CONVENIENT COLOR CAMERA

By C. M. CLARK

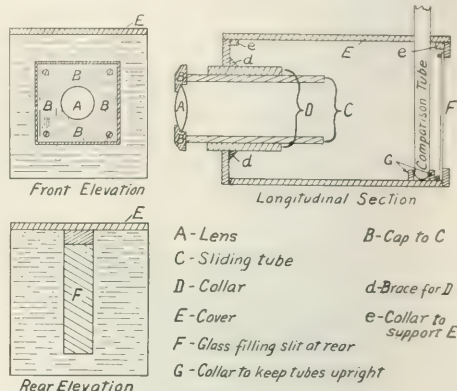
Received June 3, 1914

This camera may easily be made by any one with a little skill in carpentry and a few moments leisure, or it can be cheaply had of any cabinet maker. It has been in use in this laboratory for some time and has given satisfaction. The lens cost about 50 cents.

The box is best made of white pine. It is 160 mm. long, 100 mm. wide, and 100 mm. high, inside measure. In one end is cut a slit 20 mm. wide, extending to within 10 mm. of the inside top and bottom of the box; this slit is closed with a piece of either ground or milk glass, as preferred, but if milk glass be used it must not be over 2 mm. thick. A piece of light blue glass may be set inside the other to neutralize the yellow rays where artificial light is used. The slit must be exactly centered. In the other end, and exactly centered, is cut a hole  $60 \times 60$  mm., and in this is set a collar made of about 6 mm. material and about 50 mm. long, with about 10 mm. projecting outside the box. In this collar

slides a tube made of the same material and about 100 mm. long, carrying at its outer end a 60 mm. sq. cap in which is set a crown glass lens of approximately 160 mm. focus. The lens should be about 35 mm. in diameter and stopped down to about 25 mm.

The cover of the box is loose, and has a collar fitting inside the box to hold it in place. In this cover, exactly opposite the glass closed slit, and about 20 mm. from the edge, is cut an aperture large enough to per-



mit the two comparison tubes to enter freely, yet without play; this opening may be felt lined. A collar having a like aperture may be placed underneath it, on the floor of the box, to steady the tubes. The inside of the box is, of course, painted dead black.

The advantages of this camera are that, as the comparison tubes set exactly in front of the slit and occupy its entire width, all light passes through them, while the lens enables one to bring the tubes into exact focus; and, as only one eye is used, there is less chance of the left hand tube looking the darkest.

The sliding tube should be rubbed with graphite.

CHATTANOOGA CHEMICAL LABORATORY  
CHATTANOOGA, TENN.

### IMPROVED METHOD FOR THE DETERMINATION OF NITROGEN IN STEEL

By L. E. BARTON

Received July 7, 1914

The method usually employed for the determination of nitrogen in steel is the one first published by A. H. Allen and modified by Prof. J. W. Langley.

When operating this method as described by Blair, "Chemical Analysis of Iron," it was observed that the sample and standard for comparison, when treated with Nessler reagent, developed colors differing in quality or tone—the sample developed an orange-yellow and the standard a brownish yellow color—which renders comparison difficult and results inaccurate.

Another difficulty sometimes encountered, which makes comparison impossible, is the clouding of solutions after addition of Nessler reagent upon standing for the specified ten minutes, and is particularly noticeable with the first 50 cc. distillate, in which the ammonia

is comparatively concentrated. However, with properly prepared Nessler reagent, this latter trouble should not occur.

Experimental work was undertaken with the object of developing a more accurate method of determination as a result of which a modification of the above mentioned method was adopted. By this modification of the method, the sample and standard distillates are prepared under similar conditions, and when treated with Nessler reagent develop colors identical in quality or tone, but proportional in intensity to the ammonia present.

If the Nessler reagent is carefully prepared and works properly, the color in sample and standard will develop almost instantly and is fully developed in less than one minute. The solutions treated with such Nessler reagent remain clear or do not cloud appreciably on standing for ten minutes; however, the comparison is best made after standing one minute and all possible difficulty due to clouding avoided.

The determination is also rendered more accurate by taking a larger sample for analysis and using an aliquot part of the total distillate for comparison.

The reagents are prepared exactly as described in Blair's "Chemical Analysis of Iron," seventh edition.

[NOTE—The ammonia-free hydrochloric acid may also be prepared thus: Dilute concentrated hydrochloric acid to specific gravity 1.10 and, without addition of sulfuric acid, distil it. Hydrochloric acid of this strength distills without change in concentration. The first 100 cc. distillate from one liter of acid will usually contain all the ammonia and is rejected; the portions distilled thereafter are collected for use but must, of course, be tested as usual to make sure they are free from ammonia.]

#### METHOD OF DETERMINATION

**DISTILLATION OF SAMPLE**—In a distilling flask of 1000 to 1500 cc. capacity, fitted with separatory funnel and connected with condenser, place 40 cc. prepared caustic soda solution; add 500 cc. distilled water, and distil until the distillate gives no reaction with Nessler reagent.

Dissolve a 5 g. sample of the steel in 40 cc. of ammonia-free hydrochloric acid, and by means of the separatory funnel add the solution slowly to the contents of the distilling flask, washing in finally with ammonia-free water. Distil and collect 150 cc. of the distillate in a graduated flask. Cork the flask and set aside. Experience has shown that 150 cc. of distillate will contain all the nitrogen in the sample.

**PREPARATION OF STANDARD**—After distilling the sample—the apparatus then being free from ammonia, but containing the residue of sample and reagents—25 cc. of standard ammonium chloride solution and 150 cc. of ammonia-free water are added to the contents of the flask, and distillation continued until a standard distillate of 150 cc. is collected in a graduated flask. As before, the single distillate will be found to contain all the ammonia from 25 cc. of standard solution.

To the standard distillate is added 6 cc. of Nessler reagent; and since the standard ammonium chloride solution is equivalent to 0.00001 g. nitrogen per cc., 1 cc. prepared standard distillate is equivalent to  $\frac{25 \times 0.00001}{156} = 0.0000016$  g. nitrogen per cc. = 0.00016 per cent nitrogen on a one gram sample.

It should be noted that the preparation of a single standard distillate is sufficient for determination of nitrogen in several samples if the comparisons are being made at the same time.

**COMPARISON AND DETERMINATION**—To make the determination, 30 cc. of sample distillate (equal to one gram of sample) are placed in one of a pair of Nessler jars and the color developed by addition of 1 cc. Nessler reagent. The standard and sample are allowed to stand one minute to fully develop the color.

Into the other jar the standard distillate is run from a burette until the colors in standard and sample jars are of the same intensity; the final comparison is made after bringing the contents of the jars to the same volume by addition of ammonia-free water to one or the other.

The number of cc. standard distillate multiplied by 0.00016 gives the percentage of nitrogen in the steel.

PERCENTAGES OF NITROGEN FOUND											
No.	N	No.	N	No.	N	No.	N	No.	N	No.	N
1	0.0038	4	0.0032	7	0.0038	10	0.0035				
	0.0037		0.0032		0.0043		0.0035				
	0.0037	5	0.0043	8	0.0037	11	0.0033				
2	0.0035		0.0043		0.0040		0.0038				
	0.0035	6	0.0040	9	0.0038		0.0037				
3	0.0037		0.0040		0.0043		0.0037				
	0.0037										

The results shown in the above table indicate the accuracy of the method thus modified.

TITANIUM ALLOY MANUFACTURING CO.  
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## ADDRESSES

### THE INDUSTRY OF THE COAL-TAR DYES<sup>1</sup>

#### AN OUTLINE SKETCH

By BERNHARD C. HESSE

Received October 29, 1914

At the very beginning, it should be pointed out that the world's market in coal-tar dyes as it stands today comprises, in round numbers, 900 distinct and different chemical substances which are made by the aid of 300 products of transformation, themselves not dyes, of 10 products obtained or obtainable from coal-tar by distillation, refrigeration, expression or the like. Therefore, actually and in reality, the present coal-tar dye industry comprises no fewer than 1,200 different products and as

many or more different processes of manufacture and requires many hundred different sets of apparatus of varying capacities and of differing kinds for many hundred different operations. A manufacturing problem comprising so many independent and yet interlaced units of manufacture and production has, therefore, varied elements of complexity; to what extent this is true will appear later on.

#### THE NATURE OF COAL-TAR

In the production of coal-tar, suitable for use in the coal-tar dye industry, there is made on the average from 100 parts of coal:

72 parts COKE 6 parts TAR (liquid and solid distillate) 22 parts GAS

The gas and coke are not considered here; the distillate, amounting to 6 per cent of the weight of the coal, is the portion of these products with which we are here concerned.

<sup>1</sup> Address delivered before the Board of Directors of the General Chemical Company, in New York, October 23, 1914.

Chemists have ascertained the presence of 155 distinct chemical substances in this liquid and solid distillate or tar; these classify broadly, as follows:

SERIES	NO	SERIES	NO.
Marsh gas	45	Anthracene	5
Benzol	73	Phenanthrene	5
Naphthalene	14	Miscellaneous	13

For dyestuff production the first is negligible and the last almost so. The number of chemical elements entering into the composition of the above substances is relatively small, being five only:

CARBON    HYDROGEN    OXYGEN    NITROGEN    SULFUR

According to the combinations of these elements, we have the 5 following classes of compounds:

Carbon and hydrogen	76
Carbon, hydrogen and nitrogen	37
Carbon, hydrogen and oxygen	23
Carbon, hydrogen and sulfur	3
Carbon, hydrogen, nitrogen and sulfur	3

Rearranging these under the three relevant general series we have:

	Ben- zol	Naph- thalene	Anthra- cene	TOTAL
Carbon and hydrogen	25	6	3	34
Carbon, hydrogen and nitrogen	32	2	2	34
Carbon, hydrogen and oxygen	11	8	19	19
Carbon, hydrogen and sulfur	3		3	3
Carbon, hydrogen, nitrogen, and sulfur	2		2	2
TOTAL	73	14	5	92

Out of these 92 compounds the coal-tar dye industry uses only 9, namely:

Benzol	Phenol	Methyl anthracene
Toluol	Naphthalene	Phenanthrene
Xylol	Anthracene	Carbazol

These nine make up about from 6 to 12 per cent of the liquid and solid distillate, or from 0.38 per cent to 0.75 per cent of the coal taken, divided approximately as shown in the following chart (Fig. 1) from Dammer, "Chemische Technologie der Neuzeit," Vol. 2, p. 906. The percentages there given are as follows:

	On tar	On coal
Benzol, toluol, etc.	1.75	0.105
Phenol	0.25	0.015
Naphthalene	5.95	0.375
Anthracene, etc.	0.20	0.012

These figures are average and, therefore, illustrative only and not strictly accurate in all cases.

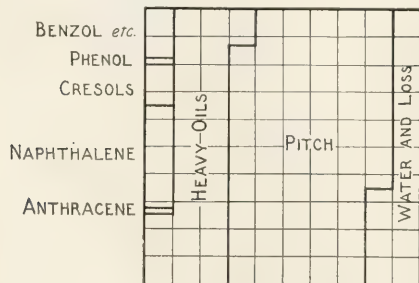


FIG. I.—MAIN CONSTITUENTS OF COAL TAR

Fig. II is a graphic representation of the above relations between the products obtained by the destructive distillation of coal and the coal itself.

None of these solids and liquids are themselves dyes; in fact, most, if not all of them, are substantially colorless and cannot impart color.

The entire coal-tar dye industry is based upon these 9 coal-tar compounds, or crudes; these 9 crudes are converted into about 300 intermediates, themselves not dyes, and these 300 intermediates are turned into 900 and more dyes.

#### THE SCOPE OF THE INDUSTRY

World's figures are not available. The most dependable and most recent figures are those dealing with Germany. In

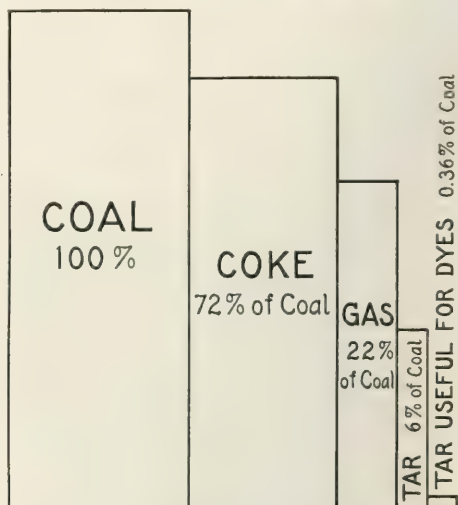


FIG. II.—COMPARISON OF COAL AND ITS DISTILLATION PRODUCTS

the year 1913 the total export value of Germany's coal-tar industry, including dyes and products of chemical transformation of the above 9 crudes themselves not dyes, *i. e.*, intermediates, amounted to \$55,264,522, distributed over 33 countries and shared in by 22 factories. On June 30, 1912, 21 of these factories had a combined capitalization of \$36,700,000 and declared and paid dividends of \$11,600,000, or 21.74 per cent of the capitalization.

Of the 5369 active corporations in Germany on June 30, 1912, 1004, or 18.69 per cent, are divided into 19 groups of the chemical and allied industries. Arranged in the order of their income-producing effects these 19 groups are, in part, as follows:

	Per cent dividends	No. of corporations
Coal-tar dyes	21.74	21
Metallurgy	11.78	61
Soaps and candles	11.65	21
Glass	11.61	38
Heavy chemicals	11.51	104
Explosives	11.22	28

The remainder range between 5 and 10 per cent except mining which is at the foot of the list with 0.51 per cent return.

Therefore, any attempt to take away coal-tar dye business from Germany means attacking the best equipped and the most profitable of Germany's industries.

PLANT VALUE—The actual cost of construction of the various plants engaged in coal-tar dye manufacture cannot be determined with any accuracy. All sorts of estimates and guesses have been made ranging from \$50,000,000 to \$1,000,000,000 with the majority in the neighborhood of \$400,000,000.

ANNUAL TURNOVER—The annual turnover cannot be determined exactly, but assuming that Germany consumes twice as much as the United States imports, we have a putative turnover of about \$80,000,000 or 2.1 times the capital stock.

The supervision and control of making this \$80,000,000 worth of product, requires at the utmost 1000 works or factory chemists, *i. e.*, on the average, one works or factory chemist for each \$80,000 of annual output.



The gross of \$55,264,552 export value is distributed over more than 900 finished dyes, each chemically different from the other and each requiring a separate though allied manufacture. This amounts to an annual average of \$61,405 for each dye all over the world outside of Germany.

However, we must subtract \$18,534,964 from the \$55,264,552 for the indigo, alizarin, anilin oil and various things, not dyes, to obtain the value of the 900 dyes which is \$36,729,588; or, an average annual world's gross, outside of Germany, of \$40,811 for each of the 900 dyes.

LARGE ITEMS OF MANUFACTURE—The large items of these 900 dyes as nearly as can be ascertained from official sources of exports are:

	Value	Per cent of total	Per cent of total exports to U. S.
Indigo.....	\$12,690,874	23.01	10.38
Alizarin.....	2,219,588	3.99	8.05
Anilin oil.....	1,408,722	2.54	33.42
Anthracene dyes.....	2,914,786	5.22	44.08
Anilin dyes.....	33,814,802	61.24	21.36
Anthracene and benzol compounds not dyes.....	1,492,736	2.72	16.22
Naphthalene compounds, not dyes.....	723,044	1.27	20.53

The dyes, including indigo, alizarin, anthracene dyes and anilin dyes, are sold to 33 countries distributed as shown in Table I.

TABLE I—GEOGRAPHICAL DISTRIBUTION OF GERMANY'S EXPORT DYE-TRADE (PERCENTAGES)

	Anilin dyes	Alizarin	Anthracene dyes	Indigo
<b>EUROPE (19)</b>				
Great Britain.....	17.14	24.34	23.72	3.34
France.....	2.15	1.59	2.52	0.97
Portugal.....	0.65			
Spain.....	1.02			0.20
Italy.....	6.38		3.23	1.98
Austria.....	8.99	3.38	6.80	4.08
Turkey.....	0.68			0.33
Roumania.....	0.35			
Servia.....	0.15			
Bulgaria.....	0.20			
Greece.....	0.10			
Switzerland.....	1.22	4.33		
Russia.....	1.71	2.83	3.17	1.30
Finland.....	0.37			
Norway.....	0.42			
Sweden.....	1.40		0.73	
Denmark.....	0.37			0.03
Netherlands.....	2.12	3.09	2.76	1.83
Belgium.....	3.90		1.96	0.94
<b>Asia (6)</b>				
Japan.....	5.48		1.63	2.46
China.....	13.17		4.44	64.03
British India.....	5.35	39.89	4.40	0.97
British Malacca.....	0.23			0.36
Dutch East Indies.....	0.58	8.41	1.49	2.86
Persia.....				0.18
<b>SOUTH AMERICA (3)</b>				
Argentina.....	0.25			
Brazil.....	0.17			
Chili.....	0.09			
<b>NORTH AMERICA (3)</b>				
Canada.....	0.69			0.25
United States.....	21.55	8.03	44.10	10.38
Mexico.....	0.85			0.05
<b>AFRICA</b>				
Egypt.....	0.34			1.33
<b>AUSTRALIA</b>				
Australian colonies.....	0.16			0.47
<b>RECAPITULATION</b>				Average participation
Europe.....	49.32	39.46	44.89	15.20
Asia.....	24.57	48.30	7.56	70.86
South America.....				37.82
North America.....	23.09	8.03	44.10	10.68
Africa.....	0.34			1.33
Australia.....	0.16			0.47
Totals.....	98.80	95.79	96.55	98.54

Germany buys small quantities of dyestuffs from six countries (probably as the United States buys eggs and butter from Canada) as shown below:

GERMANY'S 1913 IMPORTS OF INTERMEDIATES AND FINISHED DYES			
	Value	Per cent of total exports	
Anilin oil and salt.....	\$ 31,654	2.25	
Naphthol and naphthylamine.....	30,940	4.28	
Anthraquinone nitrobenzol, toluidin, resorcin, phthalic acid and other coal-tar products.....	116,620	7.81	
Anilin dyes.....	1,415,388	4.17	
Alizarin red and all other anthracene dyes.....	179,452	3.49	
Indigo.....	92,582	0.73	
TOTAL.....	\$1,866,636	3.79	

#### THE WORLD'S PRODUCTION OF COAL-TAR DYES

In 1896 the world's anilin (*i. e.*, only a part of the coal-tar dyes) dye production was estimated at \$25,000,000 distributed as follows:

		Per cent
Germany.....	\$18,000,000	72
Switzerland.....	3,200,000	12.8
France.....	1,600,000 to 2,000,000	8.0
Great Britain.....	1,600,000 to 1,800,000	7.2

This is exclusive of alizarin, anthracene dyes and of indigo.

For 1912, value figures are available only for Germany, Switzerland and Great Britain; tonnage figures for Austria. They show the following trade balance in all branches; crudes, intermediates and finished dyes, inclusive of anilin dyes, alizarin, anthracene dyes and indigo.

FINAL BALANCES, 1912		Imports	Exports
Germany.....			\$51,545,326
Switzerland.....			3,794,898
Great Britain.....		\$6,275,775	

The distribution of these balances over the various items is shown in Table II.

#### AVERAGE UNIT PRICES OF CRUDES, INTERMEDIATES AND FINISHED DYES

If the following 1912 tables for Germany, Switzerland and Great Britain are recalculated to cents per pound for each subdivision, in the case of benzol the prices per U. S. gallon are:

British export values =	16.75 cents
German import values =	24.20 cents
German export values =	19.11 cents

The average German import and export values of crudes, intermediates and finished dyes in 1913 was as follows:

	IMPORTS		EXPORTS	
	Cents per lb.	On basis of crudes	Cents per lb.	On basis of crudes
Crudes.....	2.06	1.00	2.83	1.00
Intermediates.....	12.08	5.85	10.07	3.56
Finished dyes.....	23.57	11.42	21.53	7.61

These average figures, unfortunately, give no direct insight into the true enhancement of crudes to intermediates, to finished dyes. While these crudes are as a rule of quite uniform percentage purity, yet the intermediates and the finished dyes are not; some of the intermediates contain only 60 per cent of the theoretical of the corresponding crudes, some of the finished dyes, *e. g.*, indigo, being in the form of 20 per cent pastes with water. This foregoing relationship is, therefore, directive only and not quantitative, *i. e.*, it does not represent the actual enhancement per pound of crude or of absolute intermediate to absolute finished dye. A nearer approach to true enhancement of crudes to intermediates is made further on in the case of anilin, naphthol and naphthylamine.

#### ENHANCEMENT OF CRUDES TO INTERMEDIATES

As a matter of mere calculation and making no allowance for losses, etc., 889 lbs. of naphthalene make 1000 lbs. of naphthol or of naphthylamine, and 839 lbs. benzol make 1000 lbs. of anilin oil.

Based on the averages of the corresponding German figures of Table III there is a margin of 10.40 cents per lb. of naphthylamin or of naphthol over the naphthalene cost, to take up the cost of the nitric acid, sulfuric acid, iron, muriatic acid, and caustic soda and other expenses, which amount is practically 7.6 times the naphthalene item. For anilin oil there is a corresponding margin of 6.15 cents per lb. to take up the nitric acid, iron and muriatic costs and other expenses, which amount is only 2.7 times the benzol item.

Enhancement in the anthracene series cannot be deduced from these figures.

TABLE II.—DYE PRODUCTIONS IN 1912

GERMANY			GREAT BRITAIN		
CRUDES			CRUDES		
	Imports	Exports		Exports	
Benzol and light oils.....	\$ 506,844	\$ 1,630,538	Benzol and toluol, gals.....	4,579,667	\$ 918,568
Naphthalene.....	184,450	211,106	Carbolic acid, cwt.....	162,459	1,006,008
Anthracene.....	66,402	12,138	Naphthalene, cwt.....	84,312	110,203
Phenol.....	536,928	851,802	Anthracene, lbs.....	2,938,098	37,872
Cresol.....	7,616	72,352			\$2,072,651
TOTALS.....	1,304,240	2,777,936			
INTERMEDIATES			INTERMEDIATES		
Anilin oil and salt.....	4,284	1,558,662	Anilin and toluidine, lbs.....	1,429,130	\$ 155,702
Naphthol and naphthalene.....	41,412	681,870	TOTALS.....		\$ 155,702
Anthraquinone, nitrobenzol, resorcin, phthalic acid, etc.....	106,624	1,432,998			
TOTALS.....	152,320	3,673,530			
FINISHED DYES			FINISHED DYES		
Anilin dyes.....	1,424,192	31,835,832		Imports	Exports
Alizarin.....	127,330	2,197,216		Cwt. Dollars	Cwt. Dollars
Anthracene dyes.....	120,904	3,428,866	Anilin and naphthalene dyes.....	283,876	7,025,619
Indigo.....		10,760,932	Alizarin and anthracene dyes.....	61,178	1,285,870
TOTALS.....	1,672,426	48,222,846	Indigo.....	28,302	436,138
			All other synthetic dyes.....	190	1,757
EXCESS			TOTALS.....	8,729,224	982,675
Crudes.....		\$ 1,473,696			
Intermediates.....		3,521,210	EXCESS	Imports	Exports
Finished dyes.....		46,550,420	Crudes and intermediates.....		\$1,470,774
BALANCE.....		\$51,545,326	Finished dyes.....	\$7,746,549	
			BALANCE.....	\$6,275,775	
AUSTRIA (values not given)					
CRUDES				Imports	Exports
	Imports	Exports		100 kg. Dollars	100 kg. Dollars
Distillation products of coal-tar.....	1,004	2,739	CRUDES	26,478	321,600
Carbolic (crude).....	54	159	Of all kinds.....		519
Carbolic (refined).....	170	14,965	TOTALS.....	321,600	6,517
Naphthalene (crude).....	259	15,607			
Anthracene (crude).....		1,111	INTERMEDIATES		
TOTALS.....	1,487	34,581	Anilin oil.....	12,330	241,668
INTERMEDIATES			Anilin compounds.....	7,980	399,000
Anilin oil.....	4,290	2	Benzyl chlorid, nitrobenzol, naphthol, etc.....	10,341	295,281
Anilin salts.....	4,805	2	Phthalic acid and resorcin.....	880	48,996
Nitrobenzol.....	1,242	8	TOTALS.....	984,945	138,613
TOTALS.....	10,337	12			
FINISHED DYES			FINISHED DYES		
Alizarin, anthracene dyes and synthetic indigo.....	19,382	5,635	Alizarin.....	2,167	60,676
Azo and sulfur dyes.....	46,546	133	Anilin, etc., dyes.....	6,167	407,022
All other coal-tar dyes.....	11,695	1,664	Indigo and carmine.....	716	28,640
TOTALS.....	77,623	7,432	TOTALS.....	496,338	5,452,651
EXCESS			EXCESS	Imports	Exports
Crudes.....		33,094	Crudes.....	\$315,083	
Intermediates.....	10,325		Intermediates.....	\$846,332	
Finished dyes.....	70,191		Finished dyes.....		\$4,956,313
BALANCE.....	47,422		BALANCE.....		\$3,794,898

Enhancement of intermediates to dyes cannot be stated from these figures with any approach to utility and is, therefore, not attempted.

TABLE III.—AVERAGE UNIT PRICES (CENTS PER LB.) OF CRUDES, INTERMEDIATES AND FINISHED DYES

CRUDES	GERMANY		SWITZERLAND		GREAT BRITAIN	
	Imp.	Exp.	Imp.	Exp.	Imp.	Exp.
Benzol, toluol, etc.....	3.28	2.59	No classification			
Carbolic, crude and refined.....	3.48	8.63	Average is			
Naphthalene.....	1.40	1.14	5.51	5.70	6.19	
Anthracene.....	1.29	0.78			2.03	
INTERMEDIATES						
Anilin oil and salts.....	9.19	8.80	8.89	7.96		10.29
Anilin oil.....						
Anilin and toluidine.....						
Naphthol and naphthylamin.....	12.93	10.55				
Anilin compounds.....			22.68	32.10		
Benzyl chlorid, nitrobenzol, naphthol, etc.....			12.95	31.33		
Phthalic acid and resorcin.....			25.84	54.41		
Anthraquinone, nitrobenzol, toluidine, resorcin, phthalic acid, etc.....	12.96	11.38				
FINISHED DYES						
Anilin dyes.....	24.82	23.86	29.93	31.87	24.75	
Alizarin.....		16.42	12.70			
Anthracene dyes.....	13.50	26.93				
Anilin and anthracene dyes.....	a)	a)		21.02		
Indigo.....	72.14	17.26		15.41		
Indigo and carmine.....		18.14	18.82			
All other synthetic dyes.....				9.25		

(a) Import is vegetable and dry; export is 20 per cent paste.

## GERMANY'S 1913 FOREIGN TONNAGE MOVEMENT

The 1913 metric tonnages of Germany of crudes, intermediates and finished dyes are:

Metric tons	IMPORTS	EXPORTS
Crudes.....	17,400	51,318
Intermediates.....	673	16,321
Finished dyes.....	3,238	108,680
TOTALS.....	21,311	176,319

The total tonnage movement is, therefore, 197,630. For every ton imported, Germany exports 8.27 tons; for every dollar Germany imports, she exports \$20.46.

## ESTIMATED WORLD'S TOTAL COAL-TAR DYE PRODUCTION, 1912

The export values of coal-tar dyes for 1912 at hand are:

	Exports
Germany.....	\$48,222,846
Switzerland.....	5,452,651
Great Britain.....	982,675
TOTAL.....	\$54,658,172

A very liberal estimate of the production of the principal countries is about as follows:

United States.....	\$ 3,750,000
France.....	5,000,000
Great Britain (over exports).....	5,000,000
Switzerland (over exports).....	1,000,000
Germany (over exports).....	20,000,000
TOTAL.....	\$34,750,000

This makes ample allowance for all items and gives a grand total of \$89,408,172, or practically \$90,000,000, as the very

maximum of all coal-tar dyes, anilin dyes, alizarin, anthracene dyes and the like and indigo produced by the five leading countries in 1912.

Thus the following is the *estimated* distribution of total production:

Germany.....	\$68,222,846
Great Britain.....	5,982,675
Switzerland.....	6,452,651
France.....	5,000,000
United States.....	3,750,000

with Russia, Holland, Austria and Belgium to be added. Allowing \$10,000,000 for these, which is clearly very high, makes the absolute maximum production all over the world substantially \$100,000,000. The combined actual factory or works area of the world's coal-tar dye plants probably does not exceed one square mile.

#### GERMANY'S ALLEGED DEPENDENCE FOR COAL-TAR MATERIALS UPON FOREIGN COUNTRIES

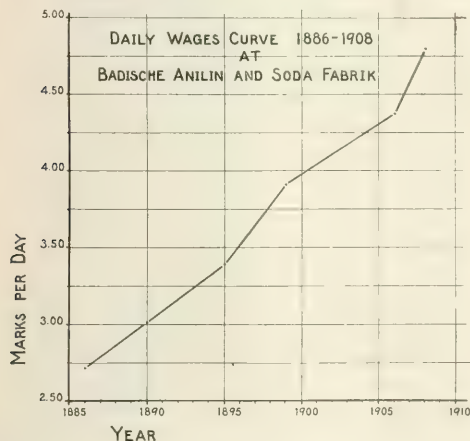
It has been urged that Germany is not wholly independent of outsiders for its coal-tar materials; possibly so. The foregoing 3.79 per cent of imports to exports may support that view.

By the same token the United States is dependent upon outsiders for hay, eggs, wheat, cotton and copper. For the years 1908-1914, both inclusive, the corresponding U. S. figures (low, average and high) are as follows:

	Low	Average	High
Hay.....	5.28	186.83	623.20
Eggs (1908-1912 only).....	1.68	6.06	12.63
Wheat.....	0.05	1.65	7.77
Cotton.....	3.19	3.60	4.24
Copper.....	24.24	31.89	36.95

#### THE WAGE QUESTION

In 1908 the average wage paid in Germany in this industry was about 4.80 marks per day inclusive of boys, common labor and skilled labor. With about 24 boys out of every 100 persons employed, and assuming each boy receives on the average  $\frac{1}{4}$  a man's pay, this makes the average man's wage M. 5.85 or \$1.40. Adding to this, \$750,000 annual welfare expense for a



total of 7000 employees and refiguring on the above ratio, makes the daily allowance for this item per man at 300 days per year 44 cents additional or a total of \$1.84, average daily adult wage. To this should be added the bonuses given to many of the workmen and also the works' contribution to the state old age pension and sick fund. Consequently, the average adult daily wage is actually in the vicinity of \$1.84.

This is reinforced by the detailed Table IV of the year 1906, wherein 40.32 per cent receive less than \$1.00 per day and 59.68

per cent receive more than \$1.00 per day of ten hours, with a grand average of \$1.04 per ten-hour day.

TABLE IV—THE BADISCHE ANILIN AND SODA FABRIK WAGE TABLE OF ABOUT 1906

Apart from bonuses, welfare expense and accident, insurance and pension fund

Daily pay in arin fac-tory cents	Aliz-ary fac-tory	Anilin dye fac-tory	Azo dye fac-tory	Acid and soda fac-tory	Indigo fac-tory	Con-struction de-part-ment	Machin-ery de-part-ment	Totals
78.5	2	23			6	8		39
80.9	1	8		2	30			39
81.3	2	31	21	50	55	2	42	203
85.8	23	52	44	81	75	49	11	345
88.2	15	39	31	72	71	3	13	244
90.5	15	49	57	72	87	36	25	341
92.9	11	32	55	72	52	5	30	257
95.3	19	30	60	72	54	73	29	318
97.7	46	35	68	64	74	15	54	356
100.1	62	70	68	73	66	161	71	571
102.4	55	48	53	71	31	26	121	405
104.8	94	78	47	41	9	36	14	319
107.2	74	58	42	37	5	19	38	273
109.6	25	16	21	21	2	15	59	159
112.0	11	13	23	19		38	67	171
114.3	1	12	12	13		71	148	180
116.7	9	2	3			18	22	59
119.1	1	10	5			93	47	155
121.5	1	6				30	19	57
123.9		3				88	35	126
126.3		2				86	29	89
128.6						95	23	118
131.0			4			107	19	130
133.4				15		31	64	64
135.8		4				19	18	57
138.2		4				28	31	63
140.5			6			2	22	30
142.9						16	13	29
145.3		4				7	21	47
147.7			6			8	19	33
150.1						6	6	12
152.4						12	19	41
154.8							6	6
157.2			5			4	6	6
159.6						6	3	9
162.0								2
164.3								2
166.7			15			8		23
176.1			5					5

Total employees 466 630 652 777 617 1170 1028 5340

Gross pay roll in dollars 620 659 740 567 1372 1166 5597

Average day pay in dollars 1.01 0.98 1.01 0.95 0.92 1.17 1.13 1.04

NOTE—These figures assume payment for ten hours only, although the men work in shifts from 6 A.M. to 6 P.M. for day work, and from 6 P.M. to 6 A.M. for night work. If the pay is for 12 hours, then each of these figures for average day, pay being based upon hourly wage-rate, must be increased 20 per cent over their present values, i. e., they would become \$1.21, \$1.18, \$1.21, \$1.14, \$1.10, \$1.10, \$1.36 and \$1.25, respectively.

#### THE INCREASED COST OF LABOR IN GERMANY

The following table presents the figures per head per working day (i. e., boys, skilled and common labor):

	Marks	Dollars	Per cent
1886	2.71	0.645	100.0
1890	3.01	0.716	111.1
1895	3.38	0.804	124.8
1899	3.91	0.926	144.3
1906	4.37	1.040	161.3
1908	4.80	1.142	177.0

or an average annual increase of 3.5 per cent of the 1886 pay.

However, it must be remembered that in Germany the day is a two-shift day with two hours and twenty minutes taken out for all men for meals and rest and for about one-third the men an additional thirty minutes for washing up; so that one-third work twelve hours less two hours and fifty minutes, and two-thirds work twelve hours less two hours and twenty minutes, or an average day of 9½ hours net actual average working time for which they receive at least ten hours pay and it may be twelve hours pay; the above figures, as stated, where based on hourly rate of pay assume pay for ten hours, only, and not for twelve hours.

In the United States the day is a three-shift day.

#### PARTICIPATION OF LABOR CHARGE IN FINISHED DYES

Labor participates to a small extent only in the final cost of the finished dye; it probably never exceeds 15 and is, as a rule, more nearly 10 per cent.

As an illustration: in 1906, Germany's export of synthetic indigo was worth about \$4,750,000; the 617 men in the Badische



indigo factory made at least 50 per cent of that export value, or \$2,374,000 worth. These 617 men represent a daily pay roll of not more than \$678.70, and it may be as low as \$567.50 (dependent upon pay being for twelve hours or ten hours); at 365 days per year this means \$247,725 or \$207,137, or 10.43 or 8.26 per cent, respectively, on half of the above indigo export value; assuming bonuses, welfare expenses and the like to double that daily pay roll, it makes the labor participation 20.86 and 17.44 per cent, respectively; however, this frees the indigo manufactured and consumed in Germany from all labor charges.

However, these 617 men no doubt in 1906 had a greater participation than 50 per cent of the export and it is, therefore, reasonable to assume that 15 per cent participation by labor in the finished product is ample and very likely high.

#### A TYPICAL GERMAN COAL-TAR DYE FACTORY

A German coal-tar dye works in good order and of considerable magnitude will have a daily use for 1000 tons of coal, 40 tons ice, 40,000,000 gallons of water (about  $\frac{1}{3}$  of Manhattan and the Bronx), 2,500,000 cu. ft. of gas.

The works area is about 500 acres, of which 100 acres are occupied by buildings, and requires about 42 miles of railway within the factory walls to transport the various materials among the several hundred factory buildings.

Power generation and transmission require 158 boilers, 386 steam engines and 472 electric motors. Over 400 telephones are needed within the works.

In order to convert the nine products obtained from coal-tar into intermediate products, and then into dyes, these works need as auxiliary chemicals: sulfuric acid, hydrochloric (muriatic) acid, nitric acid, liquid chlorine, caustic soda, carbonate of soda, acetate of soda, acetic acid, acetic anhydrid, bromine and iodine—in large amounts, which, for obvious reasons, cannot be distributed as to the total amounts produced or used.

The following figures, taken from Dr. Brunck's 1900 Indigo Lecture, may give an idea of the magnitude of some of these items; these figures are now more than 14 years old and have no doubt immensely increased; at that time the Badische Anilin und Soda Fabrik made about 50 per cent of the world's consumption of indigo. Today all the German works make practically 95 per cent of the world's consumption; it is fair to double the following figures to get an approximate notion of today's figures; 50,000 tons of sulfuric anhydrid (equal to 40,000 tons pyrites), 4,400,000 lbs. of glacial acetic acid, which require not less than 5,200,000 lbs. liquid chlorine and produce 5,850,000 lbs. caustic soda as well, and the equivalent of about 7,800,000 lbs. or 3,900 tons of commercial muriatic, and an investment of \$4,500,000.

At that time (1900) the total world's consumption was estimated at 11,000,000 lbs. dry weight (100 per cent) indigo; in 1913 Germany exported 15,000,000 lbs. (100 per cent) indigo.

The world's annual consumption of indigo is today not far from 8200 tons (100 per cent) indigo or 27 tons per day.

#### PATENTS AND THE COAL-TAR DYE INDUSTRY

The development of the coal-tar dye industry called for 8062 German patents in the years 1876–1912, or 224 per year; corresponding patents have been taken out in other countries, e. g., 2432 in the United States.

But it is authoritatively said that only 1 in 100 of the German patents is a money maker and, as a matter of fact, in the case of the 921 dyes in the world's markets at the end of 1912, only 485 U. S. patents and 762 German patents were involved, or 19.94 per cent of the total U. S. and 9.46 per cent of the total German patents. Of these 921 dyes, 50 per cent, were never patented in the United States; the U. S. patents on 26 per cent have now expired leaving 24 per cent still covered by existing U. S. patents, but many of these expire in 1915.

#### THE PRIMARY COAL-TAR PRODUCTS AND THE INTERMEDIATE PRODUCTS

The nine different crudes from coal-tar which form the basis of the coal-tar dye industry are first converted into materials, themselves not dyes, but different from the nine original compounds. These nine compounds make about 270 intermediate products and these 270, by suitable combination, make the 900 and more different dyes of the present world's markets.

The above number of intermediate products by no means exhausts those that are possible, nor do the 900 dyes exhaust those theoretically possible; there are probably over 2000 intermediate products possible, but only about 270 that have found use and there are many thousands of millions of dyestuffs wholly distinct from each other embraced in the 8,000 German patents; but of these thousands of millions of dyes only 400 individuals have survived and are of use. It is extremely doubtful that in the remainder of these millions upon millions there are any dyes of any striking utility not covered by those already in use. It is safe to say that the German coal-tar dye industry has gone over all of the known fields in fine-tooth-comb fashion and the results thereof are laid down in their patents and are shown in the goods that they market. The Germans are, of course, searching for new fields; in the last 10 years only one new field has been opened and while that is limited it promises to be of great value.

#### THE FUNCTION OF RESEARCH IN ESTABLISHING THE PRESENT INDUSTRY IN THE U. S.

Therefore, a research laboratory, in the narrow sense of the word, is not necessary for the development of a real coal-tar dye industry in the United States. What we do need is a semi-manufacturing laboratory in which to ascertain the most favorable conditions for carrying out those operations which the work of the Germans both in their patents and in their commercial exploitation of them has shown to be needful or worthy of prosecution. That, however, is no child's play task; it calls for engineering skill of the highest order, for chemical knowledge of great refinement and experimental ability of high rank. Much will have to be learned and determined as to the proper materials of construction, the proper size and shape of the apparatus and the most favorable working unit, which is by no means constant from one dyestuff or one intermediate product to another. Many dyestuffs cannot be made commercially in lots much greater than 110 pounds; others can be made in lots of one ton, but the manufacturing unit, as a rule, is small. Much of this apparatus is enamelled or homogeneously lead-lined.

Of course, the ultimate success will depend upon our merchants and our ability to merchandize against the very efficient merchandizing organization of the Germans.

#### MANUFACTURING PROCESSES

It must not be assumed that the precise manufacturing directions are all laid down in the literature, patent or otherwise. Practically all of the works keep the details of their actual processes very much to themselves. Thus, for example, one works may excel in the production of sulfonated anilin-blues; while there is nothing patented or patentable about that operation, the trade will take one factory's product in preference to any other, on looks or "aspect" alone. There are numerous instances where even these large German works with all their research facilities and with all their engineering ability have been unable to outflank an original patentee or original producer, either as to price or as to quality of the goods whose patent has expired, even years after the expiration of that patent. This has also occurred in the case of non-patented products and in one instance, at least, Americans can and do produce a dye from German intermediates and sell that dye back to the Germans at a price and of a quality the Germans cannot meet. We must, therefore, be prepared to expect that our goods would not sell in open competi-

tion with foreign makes of the same goods for perhaps one or more years after we had attempted to market them.

#### ACQUIRING PROCESSES

Furthermore, on account of the necessity of having good, careful, uniform manufacture at all points it is quite out of the question for any one chemist to acquire valuable manufacturing experience, except in only a very limited number of chemical transformations. Therefore, successful purchase of recipes or engagement of competent manufacturing chemists to make whole lines of dyes is practically out of the question although it may succeed for a limited number of dyes or operations. We shall have to rely on our own ingenuity, skill and ability to devise successful commercial methods of manufacture.

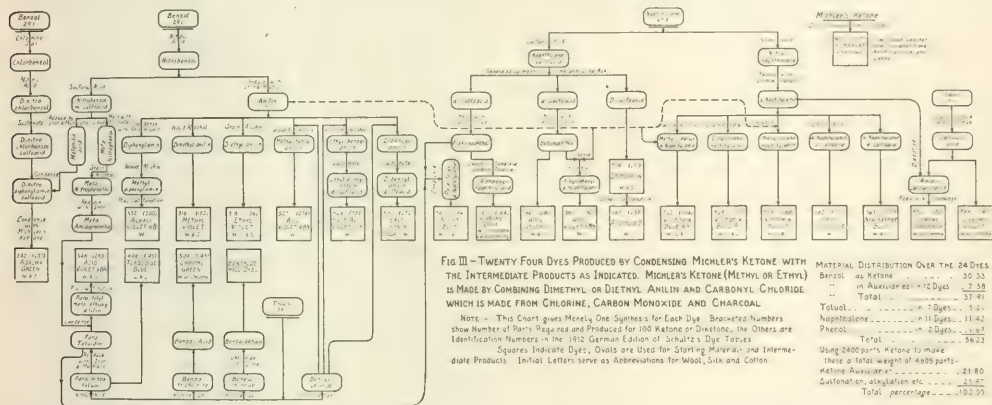
#### THE MARKETING OF COAL-TAR DYES

In 1897 the total number of different brands or commercial varieties of dyes sold by a single German concern all over the world amounted in round numbers to 8,000. Each one of these 8,000 brands has its own peculiar advantage over each of the others. These 8,000 brands, which have, no doubt, increased in number now, are used by those who use dyestuffs and produce with them thousands upon thousands of different shades and tints upon materials of the greatest diversity. This necessitates, of course, the constant production of sample cards by the

diagrams have been constructed to show in the simplest and most direct manner the genetic relationships between crudes, intermediates and finished dyes; these charts are, therefore, not to be taken as expressing all details or all possible modes or even the very best modes of making the various products and transformations. What they are intended to express is the order of production of the principal transformations and to indicate very briefly merely the outline of one way of accomplishing that change; they are indicative or directive only and are by no means to be regarded as presenting complete actual manufacturing operations or anything approaching that.

#### THE KETONE DYES (FIG. III)

This synthesis has been selected for the purpose of illustrating a group of twenty-four dyes closely related chemically, as well as from a manufacturing point of view; they are all good sellers and have been in the world's markets for upwards of 30 years with the exception of one or two which are only 8 or 10 years old. Eight were never patented in the United States. On 11 the U. S. patents have expired, on 3 the U. S. patents expire in 1915 and one each in 1916 and 1925. They represent only  $1/40$  of the entire number of dyes but exemplify and typify the interlocked and interlaced manufacturing dependency as simply as possible. Other groups are far more complex, chemically



dyestuff-makers each season of each year to show how the fashionable shades and even staple shades can be made profitably and cheaply.

#### BY-PRODUCTS

Broadly speaking, the entire coal-tar dye industry is a complicated maze and net-work of interlocking and interlacing products and by-products; these are great in number but, in most cases, small in volume individually. In numerous instances the very existence of the by-products was the sole directing cause for the invention of new dyes and classes of dyes.

#### THE DYES OF THE WORLD'S MARKETS

The 921 different dyes on the world's markets at about the end of 1912 are divided into 17 separate chemical classes as follows:

Nitroso dyes	4	Chinolin dyes	4
Nitro dyes	4	Thiobenzoyl dyes	5
Silbene dyes	10	Indophenol dyes	1
Pyrazolone dyes	12	Oxazin and thiazin dyes	48
Azo dyes	462	Azin dyes	38
Auramines	2	Sulfide dyes	52
Tri- and di-phenylmethane dyes	73	Anthraquinone and allied dyes	116
Xanthone dyes	34	Indigo dyes	48
Acridin dyes	8		
		Total	921

#### THE CHARTS OR DIAGRAMS

For present purposes of illustration a number of charts or

as well as from the point of view of manufacture and sale. Fig. III probably represents the simplest and least complex relation ships in the coal-tar dye industry.

It should be remembered that each of the 17 different classes is interlaced and interlocked with one or more other classes and that the interlacing between individuals of Fig. III is true in great and very important measure of the 17 large divisions.

"KETONE"—The starting material for the 24 dyes of Fig. III is called "Michler's Ketone" and is prepared from dimethyl anilin and carbonyl chloride. It was discovered in 1876.

Dimethylanilin is made from anilin, anilin salt and acetone-free wood alcohol; anilin itself from nitrobenzol and that from benzol and nitric acid.

Carbonyl chloride is made from equal volumes of carbon monoxide and chlorine by means of a contact agent, preferably animal charcoal; platinum has also been used. It is now said to be made chiefly by the process of Michalske (U. S. Pat. 808,100 of December 26, 1905). In this process calcium chloride is heated with lime and coke breeze in an electric furnace; the carbonyl chloride is condensed as a liquid at 8° C. (about the freezing point of benzol). The carbonyl chloride gas is passed into the liquid dimethyl anilin at ordinary temperature until the weight increases 40 per cent; the mixture is then heated to

100° C. for several hours to complete the reaction; the product is a solid melting at 174° C.

By using grain alcohol in place of the wood alcohol, above, the corresponding ethyl product is obtained. It is not so important as the methyl product. "Ketone" is the nickname applied to the product made from dimethyl anilin, and "diketone" is that applied to the diethyl anilin product.

#### MAKING DYES FROM "KETONE"

In general, dyes are made from ketone by treating a mixture of it with phosphorus oxychloride or phosphorus trichloride with another coal-tar derivative; this operation is technically known as condensing. In Fig. III the dyes are represented by squares; the material combined with ketone to produce any one of these dyes is indicated on the oval next preceding the square.

Where phosphorus chlorides are used they are generally used in the proportion of 60 to 100 per cent of the ketone taken; toluol may also be used as a diluent when the amount of chloride can be reduced somewhat.

Many modifications have been introduced as to the condensing agent; zinc chloride, aluminum chlorid, and sulfuric acid may, in special cases, be used in place of the phosphorus chlorides. In general, the phosphorus compounds are the best condensing agents in this method. They appear finally as phosphoric or phosphorous acid. What is actually done with them is not

TABLE V—DATA ON DYES OF FIG. III

No. of dye	The TWENTY-FOUR DYES	Acid	Basic	Cotton mercerized	Wood	Chrome wood	Silk	Never patented	Expiration of patent	Parts from 100
	RED									
550 (a)	Chrome bordeaux.....	x				x		x		150
YELLOW										
493 (b)	Auramine.....		x	x	x				1901	113
GREEN										
509	Chrome green.....	x				x			1900	145
542	Agaluna.....	x			x				1925	237
564	Birch green.....	x				x			1916	201
566	Wool green S.....		x		x		x	x		160
BLUE										
498	Turquoise blue.....		x	x			x	x		145
522	Victoria blue 4 R.....		x	x	x				1901	204
531	Eriocyanin A.....	x								272
558	Victoria blue R.....		x	x	x			x		170
559	Victoria blue B.....		x						1901	188
560	Night blue.....		x	x	x		x	x		184
562	Past acid blue.....	x						x		177
563	New patent blue.....		x						1915	177
565	Acid blue S.....	x							1915	239
567	Chrome blue.....				x				1910	164
VIOLET										
516	Crystal violet.....		x	x		x	x		1900	152
527	Acid violet 4 BN.....		x			x			1903	274
528	Past acid violet 10 B.....		x							279
548	Acid violet 6 BN.....		x			x			1910	293
549	Chrome violet.....		x			x			1909	145
561	Acid violet 5 BNS.....		x						1915	180
518	Ethyl violet.....		x	x	x		x		1900	156
512	Alkali violet 6 B.....		x		x				1903	200
TOTALS.....		15	9	7	17	5	11	8	11	4605

(a) Also calico printing.

(b) Also paper, leather, jute, cocoanut fiber, artificial silk and lakes.

definitely stated but their conversion into phosphorus chlorides seems feasible and obvious.

The course of materials in making ketone and condensing it may reasonably be represented as follows:

A—Carbonyl chloride (33.21) + dimethylanilin (90.31), yield ketone (100) + 100 per cent hydrochloric acid gas (21.24).

The figures in parentheses give the theoretical proportions for 100 parts of ketone; no account is here taken of losses.

B—Phosphorus oxychloride (100) + ketone (100) + intermediate material, yield phosphoric acid (11.87) + 100 per cent hydrochloric acid gas (13.25) + recoverable phosphorus oxychloride (81.47) + dye (x).

BY-PRODUCTS OF THESE 24 DYES—Therefore, in making 100 lbs. of ketone and making dye therefrom, 34.49 lbs. of 100 per

cent hydrochloric acid gas or roughly 100 lbs. of 33 per cent commercial muriatic acid are produced; of this only 30.51 per cent are usable in making the hydrochloric salts of such of the dyes made in this class as are basic; the remainder, or 70 lbs., of commercial muriatic is available for other purposes.

Table V gives relevant data as to the 24 dyes of the class here considered; of these only 9 are basic and in the case of all the other 15 the whole of the commercial muriatic producible is available for other purposes. Data as to the relative amounts produced of these 24 dyes are not available and any statement as to such relationship would have to be nothing but the baldest kind of guess.

#### THE CHEMICAL TRANSFORMATIONS

The manufacture of these 24 dyes calls for the following eleven chemical operations, each of which is briefly described below.

- |                |                   |                             |
|----------------|-------------------|-----------------------------|
| 1 Nitrating    | 5 Oxidizing       | 9 Condensing                |
| 2 Chlorinating | 6 Caustic-melting | 10 Carboxylating            |
| 3 Sulfonating  | 7 Alkylating      | 11 Diazotizing and coupling |
| 4 Reducing     | 8 Liming          |                             |

1—NITRATING—The material to be nitrated is treated with "mixed acid," *i. e.*, a mixture of nitric acid with sulfuric acid; generally only mono-nitration is effected; dinitrating and trinitrating are less frequently performed; the differences are wholly of proportions, times and temperatures. The kind or quality of nitration product is not in every respect under control but quite generally the reaction can be "steered" in the right direction. The spent mixed acid in many cases can be re-strengthened so that there is only a slight loss of sulfuric acid.

2—CHLORINATING—The material to be chlorinated is treated with dry chlorine gas (usually from the electrolytic caustic soda plant followed by liquefaction and gasification); as in nitrating there may be mono-, di- or tri-chlorinating and in addition the chlorination may be in the "ring" or in the "side chain," so, according to the material there may be six courses for the reaction to go; it is not so readily "steered" as is nitrating. In chlorinating, one-half of the chlorine employed appears as hydrochloric acid gas (100 per cent), so that for each pound of chlorine that is introduced one pound of 100 per cent hydrochloric acid is obtained, *i. e.*, 3 lbs. of commercial 33 per cent muriatic acid.

As an illustration of what this means, take Dr. Brunck's figures of 1900 wherein 4,400,000 lbs. of glacial acetic acid are chlorinated annually; these require not less than 5,200,000 lbs. of liquid chlorine and produce 3,900 tons of 33 per cent muriatic acid, or 11 tons daily. These figures are today, perhaps, doubled for the indigo industry alone. It is hardly to be expected that this amount of acid is thrown away.

Further, the above quantity of chlorine corresponds to about 5,850,000 lbs. or 292½ tons of caustic soda annually or 8.5 tons daily.

3—SULFONATING—The material to be sulfonated is treated with 98 per cent or with fuming acid, *i. e.*, oleum, according to the product desired. As a rule, the amount of sulfuric taken is several times that required to do the chemical work, the excess acting as a vehicle. Mono-, di- and tri-sulfonation may occur, and the course can be "steered" with difficulty except in a few cases. The excess sulfuric is as a general thing lost, either as calcium sulfate or as a weak and highly contaminated sulfuric acid of which a part only can be strengthened up; it is, as a rule, run into the sewer. In sulfonating, in general, much of the sulfuric doing chemical work is divided over a number of products and of these some are far less useful than others and the art of making both ends meet in this phase is dependent upon how fully these different sulfonation products can be used in dyestuff making.

4—REDUCING—As a rule, only nitro bodies (the products of nitration) are reduced; when reduced they yield amido bodies, *e. g.*, nitrobenzol yields amidobenzoil, otherwise known as anilin. Reduction is, as a rule, effected by the use of iron in



the form of powder, filings, drillings, etc., with the aid of acetic or of hydrochloric acid. The iron residue is very largely reconverted into metallic iron. The world does not use enough iron salts to make even a dent in the amount of these residues available.

**5—OXIDIZING**—This is effected largely by means of lead peroxide; manganese dioxide and also permanganates are used; hydrochloric acid is generally used in connection with them although sulfuric acid is also used. The manganese residues are generally re-worked to peroxide while the lead residue is used for lead chromate and similar articles. Potassium bichromate (residue chrome alum) and chlorate of potash (residue chloride of potash) are also used for oxidation purposes.

**6—CAUSTIC MELTING**—The substance to be subjected to the caustic melt is, as a rule, a sulfonation product, and the purpose of this melt is to remove the sulfuric acid portion and put the hydroxyl group in its place. For example, benzol mono ulfoacid yields hydroxy-benzol, *i. e.*, phenol or carboic acid; naphthalene monosulfoacid yields alpha-naphthol or beta-naphthol, depending upon which particular monosulfoacid of naphthalene was used. The sulfuric portion re-appears as sulfite of soda. As a rule, the amount of caustic soda taken is greater than that required for the chemical work; the excess is lost as carbonate in weak water solution, carrying the sulfite; this is used for bisulfite production or Glauber's salt production, or is thrown into the sewer as commercial conditions may indicate.

This process is not easily "steered," it calls for extreme care, and its success depends upon very minute details not always easily discoverable, and when discovered very conscientiously kept secret.

**7—ALKYLATING**—This is the introduction of methyl or ethyl groups into hydroxyl groups or into amido groups. Methylation is generally effected by the use of wood alcohol and hydrochloric acid under pressure in closed vessels at elevated temperatures; sometimes methyl chloride must be used. Ethylation is similar to methylation, using grain alcohol for the wood alcohol and ethyl chloride for the methyl chloride.

**8—LIMING**—This is generally applied to sulfonation products to separate the different chemical substances from each other; as a general rule the lime salt of one or more is soluble and of the other insoluble; lime or chalk may be used; generally lime is preferred on account of absence of frothing, but where that is not objectionable limestone or chalk is used. In this case all free sulfuric acid is rendered useless as sulfate of lime.

In another phase of liming, however, caustic lime is necessary, as in separating benzal chloride from benzo-trichloride; the former gives benzaldehyde which is blown off by steam and the latter gives benzoate of lime, which is further decomposed to give benzoic acid.

**9—CONDENSING**—This covers all those processes where two different substances (or two molecules of the same substance) unite to form a new compound by the loss or elimination of water or its equivalent between them; among the most common equivalents for water-loss is loss of hydrochloric acid or of ammonia.

Sulfuric acid is a common condensing agent and for this purpose is used in considerable excess; in general, it reappears as a very weak acid and is lost to the works; the other condensing agents such as chlorides of phosphorus and of sulfur, zinc chloride, aluminum chloride, antimony chloride and the like can, as a rule, be recovered in usable form and returned to the cycle at a slight additional cost.

**10—CARBOXYLATING**—This is generally performed by the action of an excess of caustic soda and pure carbon dioxide gas upon a hydroxylated, *i. e.*, phenolic or naphtholic substance; for example, phenol or carboic acid yields salicylic acid and alpha-naphthol yields alpha-oxy-naphthoic acid. Salicylic acid has wide application in the coal-tar dyestuff art. The caustic is recoverable only as a salt (sulfate or chloride, etc.).

**11—DIAZOTIZING AND COUPLING**—An amido compound such as alpha-naphthylamine on treatment with nitrous acid yields a compound called diazonaphthalene; this operation is called diazotizing. When this result is brought into contact with salicylic acid in the presence of sodium carbonate or acetate it yields a new substance; this operation is called coupling. This product on reduction yields a new compound, amido-salicylic acid, and the original alpha-naphthylamine. The amido-salicylic acid is itself very useful in the coal-tar dyestuff art.

These two operations are the most ubiquitous and widely applied reactions in the entire industry; they serve to help in making intermediate products and to produce the multitudes of substances known as azo-dyes which make up more than 50 per cent of the individual dyes of the world's market. This group of azo-dyes is a terrific and bewildering maze of interlocked and interlaced substances and operations compared with which the 24 dyes here charted are the merest alphabet of simplicity, as is shown later under the benzidine dyes.

#### MAKING MICHLER'S KETONE

In making the ketone for the 24 dyes in Fig. III, four operations are employed:

Nitrating	Reducing	Alkylating	Condensing
The following twelve materials are needed:			
Benzol	Carbon monoxide	Sulfuric acid	
Nitrobenzol	Chlorine	Iron filings	
Anilin	Phosphorus	Muriatic acid	
Wood alcohol	Nitric acid	Animal charcoal	

The product of these operations and materials is *not* a dyestuff but must be *condensed* with other products; in fact we are now only ready to begin to make a dye but only *after* we have made several other substances—to be accurate 18 additional compounds to make these 24 dyes.

Table VI shows the distribution of operations and materials over the things other than "ketone" that are to be combined with "ketone" to make dyes.

For twelve of these 24 dyes one member of the four classes of organic materials, namely,

I = Fatty series II = Benzol III = Toluol IV = Naphthalene

is sufficient; for the other twelve the following combinations of materials are necessary:

Classes	No. of dyes	Classes	No. of dyes
I and II...	4	III and IV...	1
II and III...	1	I, II and IV...	3
II and IV...	1	I, II and III...	2

The operations required are a total of 118. In Table VI "xx" indicates that the operation has to be performed twice in making one dye.

TABLE VI—MATERIALS AND OPERATIONS OF THE 24 DYES

Dye No.	Totals	I	II	III	IV	1	2	3	4	5	6	7	8	9	10	11	Totals
380	1	x													x	x	4
493(a)...	1																(a)
539	1		x														4
542	1		x			x	x	x	x	x							6
565	1			x											x		5
566	1			x													5
498	1		x														6
522	3	x	x			xx		xx					x		x		6
531	3	x	x	x				x	xx	x							7
558	1	x	x			xx											5
559	2		x	xx				xx					x		x		6
560	2		x	x				x	xx					x	x		6
562	1			x				x	xx	x							6
563	1			x				x	xx	x							6
564	1			x				x	xx					x			4
567	1			x				x	xx	x					x		6
516	2	x	x			x											5
527	1		x					x						x			5
528	3	x	x			x		xx						x			7
548	2		x	xx				x	xx				x	x			8
549	1		x														3
561	1		x												x	..	6
518	2	x	x			x							x	x			3
532	2	x	x					x							x		4
TOTALS	41	9	14	7	11	21	5	13	31	12	5	8	8	11	3	1	118

(a) No. 493 (auramine) uses double chloride of zinc and ammonia only, in addition to "ketone."

## COAL-TAR PRODUCTS PARTICIPATION IN THE 24 DYES

In making the quantities of each of the 24 dyes given in Table V the material participation is as follows:

	Per cent
Ketone.....	52.11
Benzol.....	5.38
Toluol.....	5.21
Naphthalene.....	11.42
Phenol.....	1.69
Sulfonation, alkylation, etc.....	25.90
	21.97
TOTAL.....	99.98

Of the ketone 52.11 per cent are benzol so that the benzol participation in the 4605 parts of the above 24 dyes is a grand total of 37.91 per cent. That is, of the 4605 parts of these 24 dyes:

	Per cent	Per cent
Benzol.....	37.91	...
Toluol, makes up.....	5.21	...
Naphthalene.....	11.42	...
Phenol, makes up.....	1.69	...
TOTAL.....	56.23	...
Ketone production makes up.....	21.80	...
Sulfonation, alkylation, etc., make up.....	21.97	...

It must not be forgotten that these 24 dyes are by no means made and sold in the proportions given in Table V. Therefore, in order intelligently to plan a works for these 24 dyes it must be known how these 24 individuals are to be distributed over the whole production in order to avoid waste of space, apparatus, material and time in laying out the relative position of buildings and their respective sizes.

## MAKING THE TWENTY-FOUR DYES

To carry out the 118 operations it is not intended to say that 118 sets of apparatus are necessary; the different sets of apparatus are 11 or a multiple thereof and how great that multiple is depends upon the relative amounts of each of the 24 dyes to be made and the time at which they must be manufactured. Further, one and the same apparatus is not necessarily adapted for any one operation on different compounds, *e. g.*, nitrating each of the three different materials to be nitrated, namely, benzol, toluol and naphthalene; nor will the same chlorinating apparatus do for all kinds of chlorinating, nor the same condensing apparatus for all condensations and so on through the list.

## UNIFORMITY OF PRODUCT

It must be borne in mind that Fig. III does not in any way attempt to show the different manufacturing operations and steps that are necessary to accomplish the indicated results; neither is it attempted to show on Fig. III the filtering operations, the precipitation operations, the blowings off with steam and other means of mere mechanical separation; between each and any two successive chemical alterations there are one or more mechanical operations not indicated, as well as secondary chemical changes such as the conversion of sulfo-acids into salts; bases into salts; the separation of the salts from their liquids and their purification, their drying, their storing. In addition to all this, of course, there is the large amount of testing that must be done at all stages of each operation and the exhaustive and careful test of each lot of final product before it is passed from one step to the other and of the finished dye before it is placed in the warehouse. The number of these operations is merely a matter of calculation and consideration but such a presentation would add nothing of moment for present purposes; on the contrary it would make Fig. III so complicated as to rob it of most, if not all, of its utility. Suffice it to say, that the tests are in many cases rapid and short but in other cases and particularly in the case of the finished products they are very refined, allow but a small margin for error or variation and require a great deal of care and painstaking in their execution. For example, in making beta-naphthol some alpha-naphthol is always formed and the users of beta-naphthol have become so refined in their requirements and demands that if a sample of beta-

naphthol carries more than  $\frac{1}{500}$  per cent of alpha-naphthol, that is, one part of alpha-naphthol in 50,000 parts of beta-naphthol, it stands a very good chance of being rejected. In making alpha-naphthol some beta is always formed and its presence in alpha is just as objectionable as is the presence of alpha in beta.

Therefore, not only are there a large number of operations, but these operations while not always under accurate control must, nevertheless, be carried out with great refinement and great exactitude and with great uniformity of final product in the majority of the cases; there are a number of cases where such refinement is not necessary but, needless to say, works that make only the rough goods could not hope to survive in competition with works that make both classes of goods. The buyers of dye-stuffs, as a rule, subject the purchased goods to severe tests and even if they do not, the competition between the various makers of dyestuffs is so keen that they themselves have effectively and effectually raised the standard of the goods to be made.

That this industry is complex, interlaced and interlocked not only from the manufacturing point of view but the merchandizing viewpoint also must be clear from Fig. III which purports to present in the sketchiest of outline the inter-relationship of only  $\frac{1}{40}$  of the individuals of the industry.

## INTERLOCKING AND INTERLACING

In Fig. III there are several instances of the production of two or more things side by side in one and the same operation and all of these must be utilized somewhere in the works in order not to be a dead loss.

Take, for example, treatment of toluol with chlorine; three substances are unavoidably formed: benzyl chloride, benzal chloride and benzo trichloride in greater or lesser proportions. In Fig. III benzyl chloride is used in three dyes, benzotrichloride in one dye and benzal chloride in a group of dyes, itself much larger than this particular group of dyes; but each of these three compounds has uses in other dyes and groups of dyes. Merchandizing effort must be directed to keeping the products of all these three materials in alignment so that excess production of none takes place over market requirements. It is a much more complicated merchandizing operation than, for example, the alignment of the salt-cake and muriatic acid markets, and still it is easier in some respects because of the greater number of outlets available. Nevertheless, it is a task requiring great skill and much careful and painstaking attention.

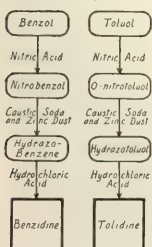
In treating toluol with nitric acid only one product is shown, namely, the para variety; however, another variety is also formed—the ortho variety which is commercially far more important than the para variety. In effect, therefore, the utilization of the para variety in this and other classes of dyes is merely making use of a substance unavoidably a by-product from another manufacture (*e. g.*, toldine manufacture) so as to avoid useless waste and loss; if one maker does not the other will and thereby gain a commercial advantage. For example, the ortho variety is used in toldine making and the para variety in magenta making (see Fig. VIII); both produce para and ortho respectively, in addition, which they respectively cannot use but *together* they can consume all of each *provided* their respective sales are properly adjusted; if not, additional uses are needed.

Other examples of such interlaced, interlocked simultaneous results are shown on Fig. VI; for example, the sulfonation products of beta-naphthol where one monosulfoacid and two disulfoacids must be kept in line; or the sulfonation of beta-monosulfoacid by means of oleum where at least two products, one disulfoacid and one trisulfoacid must be managed; direct loss of product with no use in this class is shown in the treatment of beta-monosulfoacid with nitric acid as described later on.

Study and examination of these charts or diagrams will dis-

close more and more how really intricate and complex as well as interdependent are these products. Nevertheless, simple inspection of these charts shows a real and important interlocking and interdependence of not only the intermediates but of the finished dyes themselves.

In Figs. IV, V and VI are presented the diagrams for 82 additional dyes and their needed intermediates; these 82 dyes are themselves important and large sellers. With the 24 ketone dyes just described they make up one-eighth of the individuals of the present world's market. The complex nature of the relationships of the relevant intermediates is obvious at a glance.



THE BENZIDINE DYES -FIG. IV

About one-tenth of the individual dyes on the world's markets have benzidine as a substantial and necessary ingredient. This can be made from nitrobenzol, caustic soda, zinc dust and hydrochloric acid and requires three chemical transformations, beginning with benzol as shown at Fig. IV. Benzidine itself,

FIG. IV-BENZIDINE AND TOLIDINE DIAGRAMS

however, is no dyestuff and, unlike anilin, it cannot be used for the production of black or any other shade upon fiber without the cooperation of some other coal-tar product. The benzidine must first be treated with nitrous acid to form its tetrazo-compound which is itself then combined with other coal-tar derivatives to produce finished dyes. In the production of the 82 benzidine dyes in the world's markets the materials or finished intermediates with which the benzidine is to be combined,

The original treatment of naphthalene, Fig. VI, is divided into three classes, namely, by nitric acid, by oil of vitriol and by fuming sulfuric acid. The nitric acid treatment followed by other suitable treatments yields 5 of these finished intermediates. The oil of vitriol treatment coupled with caustic melt, nitric acid treatment, reduction, treatment with nitrous acid and heating with water or with oil of vitriol yields 21 of these finished intermediate products; the treatment with the fuming acid yields but one finished intermediate.

When these 44 compounds are combined with benzidine to produce the 82 dyes, they are used two at a time, three at a time and four at a time or each one twice and it is self-evident from the possible permutations and combinations that there is a wide field opened up by these 44 finished intermediates; however, only 82 individuals have been found to be of lasting commercial value.

The benzidine dyes, which are valuable because they are direct cotton dyes (that is, dye cotton fiber without the use of a mordant), are incomplete of themselves for the commercial range of shades and colors in this class of materials and as a complement the tolidine dyes are employed. Tolidine is made from nitro-toluol (the ortho variety) in the same manner that benzidine is made from nitro-benzol (see Fig. IV). Tolidine, in turn, is combined with finished intermediates as is benzidine but requires finished intermediates over and above those shown on these charts and their genetic relationship is quite as complicated as that shown for the benzidine finished intermediates. Of the above compounds found in coal-tar only two are useful as such for union with benzidine and tolidine; they are phenol and cresol but the role they play in that capacity is rather subordinate.

The number of intermediate steps from naphthalene (Fig. VI) to finished intermediate is at a maximum in the case of 2.7

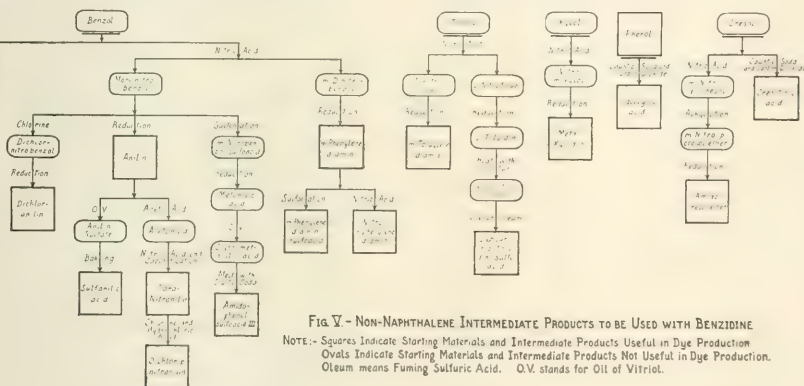


FIG. V - NON-NAPHTHALENE INTERMEDIATE PRODUCTS TO BE USED WITH BENZIDINE  
NOTE: - Squares Indicate Starting Materials and Intermediate Products Useful in Dye Production  
Ovals Indicate Starting Materials and Intermediate Products Not Useful in Dye Production.  
Oleum means Fuming Sulfuric Acid. O.V. stands for Oil of Vitriol.

number 44. These 44 compounds are made from benzol, toluol, xylol, phenol, cresol and naphthalene and the making calls for the intermediate production of 55 substances that have, so far as these dyes are concerned, no other use than to serve as intermediate products.

Benzol, Fig. V, is treated with oil of vitriol or with nitric acid to form two different classes of benzol derivatives, the former having but one member and the latter having 9; toluol on treatment with nitric acid and three separate additional chemical treatments yields two finished intermediates. Xylol on treatment with nitric acid yields but one finished intermediate. Of course, other operations are necessary, such as the caustic soda melt, sulfonation, reduction, chlorination and baking. Phenol on carboxylation yields salicylic acid, and cresol on carboxylation yields cresotinic acid and on treatment with nitric acid and subsequently by alkylation and reduction yields amido cresol ether.

di-amido naphthalene 3,6 disulfo acid; in that case six intermediate products must be prepared, no one of which has any use in this class of dyes, other than the production of this one finished intermediate. None of these starting materials yields a finished intermediate with one chemical operation except in the case of phenol and cresol; for all others at least two chemical steps must be taken before a finished intermediate is arrived at.

In addition to benzidine and to tolidine, 6 other substances of a similar nature are employed to complete this commercial series of direct cotton dyes and they in turn make use of some of these finished intermediates and in addition others not here charted.

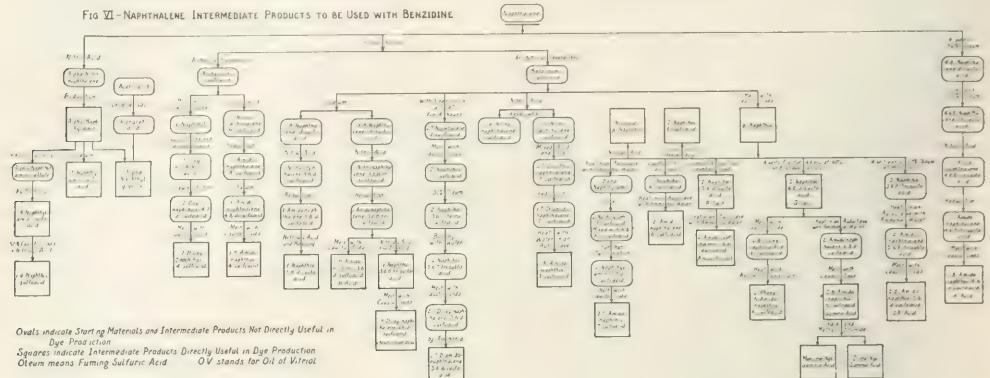
Going back on Fig. VI, to the treatment of naphthalene beta-monosulfoacid with nitric acid it will be noted that the chart states that two nitration products are formed in equal parts; so far as this particular class of dyes is concerned one of those equal parts of nitration product is useless. It becomes a burden



to the other part so that the 1,5 di-amido naphthalene 7 sulfoacid must bear the entire cost of nitrating the beta-mono-sulfoacid although only one-half of that nitric acid and one-half of the beta-mono-sulfoacid is available for it; the other part

syntheses are divisible into 2 classes; three of them start from benzol and the remaining one starts from naphthalene and they all come together at the indoxyl point and from that point are all substantially identical. The salient point is at the pro-

FIG VI.—NAPHTHALENE INTERMEDIATE PRODUCTS TO BE USED WITH BENZIDINE



goes to form a waste heap unless utilized in some other branch of the industry.

The 167 direct cotton dyes of the diphenyl type of the present world's markets are distributed as follows, among the various diphenyl derivatives:

Benzidine .....	82	Benzidine-mono-sulfoacid .....	2
Tolidine .....	43	Benzidine disulfoacid .....	4
Dianiline .....	28	Ethoxy-benzidine .....	4
o-Nitrobenzidine .....	1		
Di chlorbenzidine .....	3	TOTAL .....	167

#### INDIGO

Four of the principal methods of making indigo have been charted (Fig. VII). In all processes of making indigo the chief difficulty has always been in getting a proper yield of indoxyl; the preparation of the glycine from which the indoxyl is made

duction of indoxyl. The method first to be used successfully commercially was to melt the glycine with caustic soda; when starting from anilin the yield rarely exceeded 45 per cent; an for a long time no means was discovered for producing any substantial increase in that yield; admixture of burnt lime to the caustic soda was tried without materially increasing the yield. Moreover, all methods that started from benzol had to take account of the possibility of the drawback that to produce enough benzol to make the world's requirement of indigo would pile up such an amount of toluol that the industry simply could not use it and the indigo would have to bear the burden of the unused toluol. That is one of the primary reasons why the naphthalene method was the first to be used successfully commercially; further, the variety of glycine producible thereby was converted into indoxyl by melting with caustic alkali to an extent approaching 90 per cent of the theory; also the amount of naphthalene required to produce the world's consumption of indigo could be obtained without entailing the use of additional and other coal-tar hydrocarbons; i. e., there was plenty of naphthalene looking for a market and while there was enough benzol available, every time a certain additional amount of benzol was used, a certain amount of toluol was produced for which a market had to be created or be a burden to the indigo. However, in the last 15 years those conditions have changed; uses of toluol have been found and it is very likely that benzol will serve as the starting point for most of the world's indigo in the future.

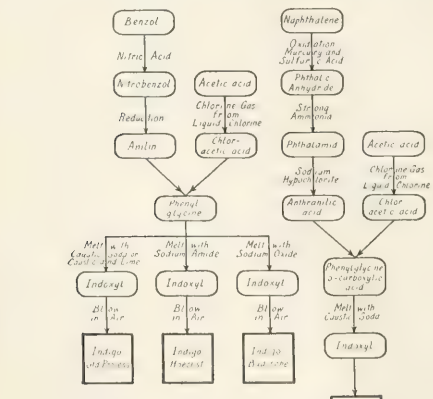
However, it was not cheap benzol and it was not the finding of a use for toluol that made benzol feasible as a commercial starting point for indigo. The discovery that sodium amide would convert the glycine into indoxyl practically quantitatively was the particular event that made the use of benzol commercially feasible; sodium oxide has also been found to be a substitute of equally good quality for the sodium amide. Reverting to Fig. VII it will be of interest to note that the first step from naphthalene to phthalic anhydride today calls for the production of an amount of sulfuric anhydride equal to 80,000 tons of 50 per cent pyrites per annum. The step of passing from acetic acid to chlor-acetic acid today calls for over 9,000,000 pounds of glacial acetic acid and over 10,000,000 pounds of liquid chlorine.

#### AMERICAN ATTEMPTS TO DEVELOP A DYE INDUSTRY—FIG. VIII

The hydroquinone diagram in Fig. VIII illustrates what American manufacturers have been doing with domestic benzol; it requires a total of four chemical operations and produces two

FIG VII.—THE INDIGO DIAGRAMS

Showing Present Commercial Processes



has in itself not offered any very great difficulty but the strategic point of the whole indigo synthesis is at that conversion, and it is at that point that most of the energy of chemists has been expended. It would not be at all surprising if on examination it were to turn out that at least 50 distinct and different modifications of operations at that point have been patented and of these probably not more than 3 survive to this day. These 4 indigo

compounds, each of them usable as such, *i. e.*, anilin, used for the production of black on cotton without the aid of any other coal-tar product and hydroquinone, used as a photographic developer. This diagram will give some measure of the difficulties that may be expected in an attempt to develop the finished intermediates necessary for the production of the 24 ketone dyes of Fig. III and the 82 benzidine dyes of Figs. V and VI.

*Magenta* requires benzol and toluol; the former must be converted into nitrobenzol and then into anilin and the latter into nitrotoluol (largely the para variety) and then reduced to toluidine by taking a suitable mixture of anilin and toluidine with nitro-toluol or nitrobenzol (as indicated in Fig. VIII), magenta base is produced, and this, on treatment with hydrochloric acid, yields the hydrochloride which is the commercial form of magenta.

A book of over 280 pages was published in 1889 and contained plates and drawings of apparatus and lay-out of works and minute directions for magenta manufacture; even this and the absence of all patents has not enabled American manufacturers to make this product in competition. It is true that magenta is still made in this country but it is made almost entirely from magenta base imported from abroad. Roughly and approximately speaking, in \$80,000 worth of magenta there are \$450 worth of commercial muriatic acid. The remainder of the value is made up by the magenta base.

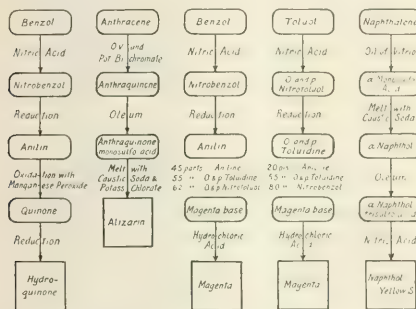


FIG VIII—SYNTHESES OF SOME DYE-STUFFS ALL EXCEPT ALIZARIN ATTEMPTED IN THE UNITED STATES AND DRIVEN OUT BY FOREIGN COMPETITION

The Naphthol Yellow S patent has been dead for over 17 years and yet none of this dye has ever been successfully manufactured from naphthalene in this country. Whatever has been manufactured in this country has been made from alpha-naphthol-trisulfoacid, imported from abroad, which is merely treated here with nitric acid and carbonate of soda and even that manufacture has now disappeared almost entirely.

*Alizarin* manufacture involves three chemical transformations of anthracene which has always been as cheaply laid down from England in the United States as in Germany; the reputation of alizarin as a money-maker and money-getter has always been world-wide, and the United States has always been a good consumer of alizarin, yet no concern in this country has ever taken up the manufacture of alizarin. It is possible that the fact that alizarin never was protected by tariff may have prevented any such effort; certainly with the patent dead for 28 years it cannot well be urged that patent rights have stood in the way.

Many of the other dyes said to be made in the United States are made in just about the same way as the Magenta and Naphthol Yellow S; that is, the bulk of the chemical work is carried out in Germany and merely the finishing touches (the "as-

sembling") is done in this country. Obviously the bulk of the profit is not in the "assembling."

#### WORKING CLAUSES

These two examples show very clearly how a working clause in the patent law does not necessarily produce a coal-tar dye industry. The patent is taken out on the commercial form and any product prior to the commercial form is *not* the subject of the patent. It requires no lengthy dissertation to show that merely putting on the finishing touches is a long ways from a true industry. France has had a working clause for a great many years, Great Britain for only seven, yet neither country today can make its dyestuffs simply because they have both been purchasing from Germany materials which bear the same relationship to the finished product that magenta base bears to commercial magenta and alpha-naphthol-trisulfoacid bears to Naphthol Yellow S. A true industry requires making all materials from the crudes.

#### GEOGRAPHY OF THE GERMAN DYE FACTORIES

In Germany the coal-tar dye plants and the principal coke oven districts are all contained within an area described by a square 300 miles on each side (see map). With but one exception the really important ones are all along the Rhine or a short distance up its tributaries. This whole district could be put inside the State of Wyoming, is much smaller than the state of New Mexico, or is smaller than New York and Pennsylvania combined. With cheap water routes and short rail hauls for the transportation of materials from one factory to another or to sea port, these dyestuff factories are most advantageously located and with the added short rail and water hauls to them from the coke regions the transportation of the raw materials to the dyestuff works is economically profitable.

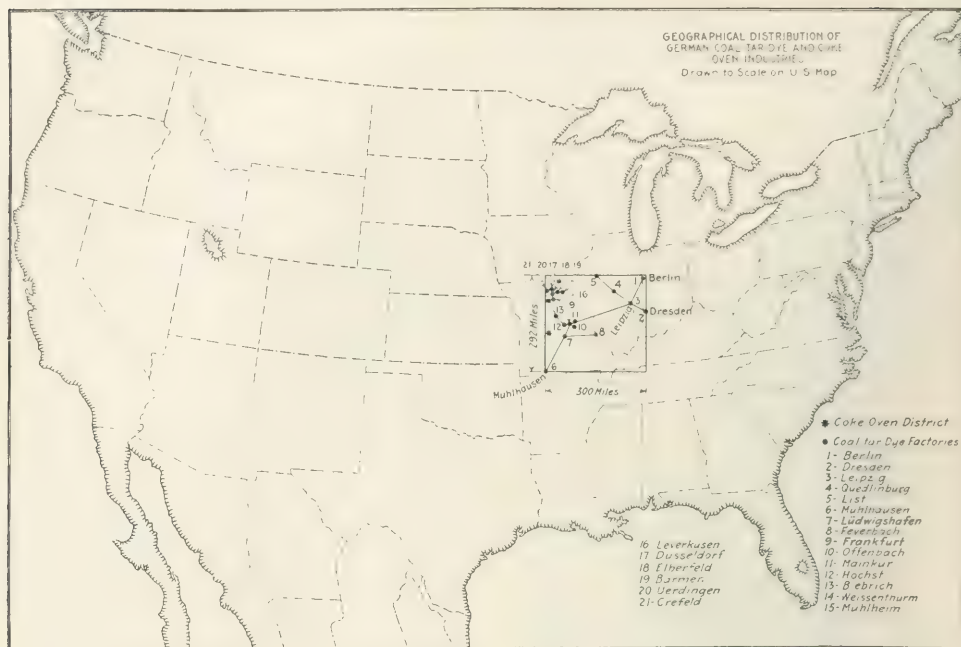
#### WHY GERMANY CONTROLS THE COAL-TAR DYE BUSINESS

The average annual unit gross per year of the 900 coal-tar dyes, exclusive of alizarin and indigo, all over the world outside of Germany, has previously been shown to be about \$41,000. Add to this the interlocked dependence of intermediates and finished dyes just shown and the facts that the German works have long ago fully paid for their plants, their experience and their sales organization and the result is what seems to be a complete answer to why Germany controls the world's coal-tar dye market. In fact, the whole industry, taking everything into account, is just about a one-nation business. It is a business made up of a large number of small units with all units essential to success.

Germany has this business established in 33 other countries; it is evident that any country starting in now would be greatly handicapped thereby if it attempted to enter the race for the full distance.

Although Germany has relied upon Great Britain for its crudes, *i. e.*, its benzol, its toluol, its naphthalene and its anthracene, up to the middle of the 90's and perhaps later, England has not been able to make any headway as competitors in dye manufacture, but on the contrary has lost ground. Many of these non-patented world's dyes are also non-patented in England yet most of Great Britain's requirements of those materials have always been supplied by Germany.

The answer to the question as to why Great Britain has not succeeded against Germany cannot be that Great Britain is not a nation with highly developed chemical industries. A German chemist as well equipped as any other living man to express an opinion and to compare German industries with British industries has said the following: "To be sure, we know that several of the European countries, *e. g.*, England, are still ahead of us in many branches of the chemical industry, especially in inorganic manufacture. But in no country on earth are those branches of the chemical industry which demand versatility of thought, and particularly a large body of scientifically trained employees, so well developed as with us. Our



synthetic dye, synthetic drug, and perfumery industries are foremost throughout the world, and there is probably no country in which the heads of factories are so imbued with the conviction that their employees must needs cast a glance beyond domestic boundaries."

Each one of the large chemical manufacturing countries of Europe, without exception, buys more intermediate products from Germany than it sells to Germany and all of the countries but one, namely, Switzerland, buy more dyestuffs from Germany than they sell to Germany. In other words, and broadly speaking, all the rest of the world, outside of Germany, merely assembles intermediates purchased from Germany, into finished dyes; Germany alone makes all its own intermediates; that is, Germany makes all the dye-parts and the rest of the world merely assembles these dye-parts into finished dyes. Needless to say, the one who controls the manufacture of dye-parts actually controls the manufacture of dyes.

Where Austria, Belgium, France, Great Britain, Italy, Russia and Switzerland singly and combined have failed, in spite of their other large chemical industries, to take away this business from Germany, the American chemist should not be blamed nor found fault with because he has not succeeded, nor should it be assumed that transplanting of the whole industry can be done at once and is a perfectly easy thing to do, as so many seem to think. The transplanting of that industry out of Germany is an undertaking properly and fitly to be described as titanic.

Why the other countries have failed is probably due to the fact that they contributed little or nothing to the real upbuilding of the business, and to its creation, for the coal-tar dye business is a *created* business; those who aided in its creation were first in the position to reap the benefits—an advantage they have no doubt earned and deserved through the effort they expended and the risks they assumed.

#### GERMANY AND THE UNITED STATES

In 1913 Germany had for sale to foreigners \$3 worth of these products as against every dollar's worth that it needed at home; the total coal tar dye imports of the U. S. constitute less than 0.4 per cent of our entire import business.

Nine hundred different dyes were on the United States markets of which 100 were made or assembled in this country from intermediates purchased from Germany. Yet these 100 do not seem to be enough for American dye-users.

How much less than the full 900 will satisfy American users is known to them and to the importers. The latter cannot be expected to divulge that information; if the former want substantial help from American chemical makers they must divulge that information; no other way of ascertaining it is available.

In 1909 the United States produced \$3,462,436 worth of artificial dyes which are probably anilin dyes in the strict sense. Compared with Switzerland's \$3,200,000 production, *i. e.*, "assembly," in 1896 this is an achievement of which Americans need not be ashamed. The wonder is not that we have not done more but that in the face of the well organized manufacturing plants of Germany and of Germany's very much superior facilities for foreign trade, both banking and carrying, that we have done as much as we have. Blame should not be parcelled out for what American chemists have not done, but credit, which has been withheld so far, should be given for what has been done in spite of obstacles abroad and obstacles at home. The users of dyestuffs have invariably opposed any tariff enactment that would substantially encourage a domestic production of coal-tar dyes. That so many are produced in this country as are being produced is due to no coöperation of dyestuff users but has been accomplished in spite of their obstruction and if today the users are in serious difficulty through a lack of dyestuffs they have their own shortsightedness to blame and cannot, by any argumentation whatever, shift the blame to American chemists.



With proper help and encouragement the American chemist will be able to increase the domestic production of coal tar dyes and to inaugurate the making of intermediates; in the course of time this country may then ultimately look forward to a substantial share of the world's coal-tar dye business.

Hardly any of the valuable or useful intermediates ever were patented. A considerable number of non-German chemists have invented and patented finished dyes made from non-patented intermediates. These inventors had perfect freedom to make the needful intermediates and an *exclusive* right to make, sell and use their new dyes therefrom, yet they bought their intermediates from Germany rather than make them themselves. The patent situation is, therefore, really, that Germany excelled the rest of the world in making patentable combinations from non-patented and non-patentable intermediates and further in making those intermediates in open competition with the rest of the world. So, from one point of view, it appears that the rest of the world, inclusive of the United States, lay back, let the Germans do all the hard work and when the rest of the world finally woke up to the value of what the Germans had accomplished they became very busy making excuses and explaining instead of making a determined, directed, united and effective attempt to recover the ground so lost. That such recovery will require the hardest kind of work on the part of all—users, capitalists, consumers and makers alike—is self-evident and obvious and the question is: Do we want to pay the price? It can be done, if the price be paid.

90 WILLIAM STREET, NEW YORK CITY

#### GAS MANUFACTURE FROM THE POINT OF VIEW OF PHYSICAL CHEMISTRY<sup>1</sup>

By W. F. RITTMAN

In past practice, gas manufacture has been primarily an engineering problem, with the chemist a more or less necessary adjunct for the analysis of coal, coke, oxide, etc. The research chemist, who deals with the processes of manufacture and the phenomena of reactions involved, has been looked upon as a burden unwarranted by returns. In view of the present available raw materials for gas manufacture on the one hand, and the demands of the public on the other, the advisability of continuing the policy of the past becomes a serious question.

There are few industrial operations which, from the standpoint of physical chemistry, are more complex in their nature than the treatment by heat of coal, oil and water in the production of coke, gas, tar, ammonia and cyanogen. In gas manufacture practically all the variables of chemical phenomena are involved. While this fact greatly complicates such industrial problems theoretically and practically, at the same time it greatly enlarges their possibilities; it strongly emphasizes the need of continued scientific research and investigation in connection with them. The heat treatment of coal, oil and water necessitates dealing with the chemical reactions of solids, liquids and gases, and with all the laws, both physical and chemical, which govern these reactions. The finest equipment in the world, designed with utmost mechanical precision, but without regard for the laws which govern the reactions carried out in it, is likely to be less useful than apparatus of the most wretched mechanical construction, but which does consider the chemical changes involved. Obviously, the aim of any industrial operation is perfection, both of process and apparatus.

Problems that are primarily chemical, and which can be attacked most efficiently from a chemical point of view, are common enough in gas manufacture. Who of the gas men present have not, at some time or another, faced the problems resulting from naphthalene, drip oil, fluctuating candle power, deposited carbon, ammonia, sulfur, cyanogen, or any one of a dozen other

<sup>1</sup> Presented with permission of the Director of the Bureau of Mines before the Chemical Section of the Ninth Annual Meeting of the American Gas Institute, New York City, October 22, 1914.

facts? Further, every new development in gas manufacture will create new problems. Every improvement will involve some question or questions peculiar to it. The greater the number of researches, the greater is the progress in a given field, and the greater becomes the number of new problems.

Hitherto, the greatest progress in American gas manufacture has been made along mechanical lines, and, as Americans, we may be proud of this progress. Chemical development, however, has been far behind the mechanical and operative improvements. It may be said that we have been spending too much of our energy investigating the machine rather than what is going on inside of the machine. Were the machine the end product of vital importance, improvements of this character would be unquestionable but the gas factory of the future will earn, or fail to earn, its dividends as it turns out, or fails to turn out, the best relative yields of coke, gas, tar and ammonia. It is true that the machine and the process are vitally related; there may be objections to this point because engineers are constantly working to perfect processes. It seems in gas manufacture, however, that too many of the purely theoretical chemical problems have been left to the mechanical or erecting engineer for solution. A mechanical, electrical or civil engineer, whose primary profession is the building and operation of machines and equipment, whose academic training consisted in the study of chemistry and physics during a part of two years, should not be expected to be as efficient in chemical research as the man who devoted himself exclusively to the study of chemical and physical phenomena; it is the latter, furthermore, whose primary profession to-day is the study of chemical and physical phenomena. To carry out high-grade research and investigation in any line, well-paid specialists must be employed. The able and efficient chemist and chemical engineer can do better things than analyze coal and iron oxide, however efficient he may be at the latter.

The day is past when gas-making is primarily a mechanical operation. Carbureted water gas constitutes approximately two-thirds of the gas made to-day, and it is no longer possible to buy a high-grade paraffin gas oil for 3 cents a gallon. Consequently, the petroleum supply becomes a most vital and important problem to the American gas manufacturer to-day. The importance of the oil problem as related to gas manufacture can be conveyed by the fact that in 1913 Greater New York alone used approximately 3,860,000 barrels of oil in the manufacture of carbureted water gas.<sup>1</sup> During 1913 the same plants used approximately 1,600,000 tons of coal. On the basis of heat units involved, oil has become as important in American gas manufacture as coal. Furthermore, Greater New York constitutes but one center for gas manufacture. I need not elaborate on the importance and seriousness of this oil problem, because you are fully acquainted with it. During the last decade, the increasing price of oil for gas manufacture has created what many gas men regard as a "dangerous" situation; and this is true despite the fact that never before in the history of the United States has so much oil been produced as to-day.

Why is it, then, that gas oil is expensive? Why should hundreds of millions of dollars' worth of oil-carbureting machinery be threatened? What is it that makes the economical use of petroleum one of the chief problems of the gas manufacturer? It is, first, the scientific progress in petroleum refining, and, second, the changing character in composition of the oil from newly discovered fields. Through careful scientific investigation, and through the application of physical-chemical principles, pure and simple, the refiner has perfected processes whereby the oil which you used to buy at 3 cents a gallon is now converted into gasoline and other end products which sell at several times that price. A representative example of this progress can be

<sup>1</sup> *Gas World*, 61 (1914), 76.

had from the testimony of Mr. Frank B. Lewis,<sup>1</sup> Jr., Manager of the Standard Oil Company Refinery at Whiting, Indiana, regarding the Burton process; this was offered at a recent court hearing in Chicago:

"Q. Your Whiting plant is running exclusively on Mid-Continent oil, is it?

A. Yes, sir.

Q. Now tell us, Mr. Lewis, what percentage of the crude oil is refined into gasoline?

A. With the present method of distillation you can refine it all into gasoline if you wish to.

Q. The entire percentage?

A. You can take it all and convert it all into gasoline, except what coke is left in the still, and a little wax or petroleum tailings.

Q. How long has that method been in use?

A. About one year.

Q. Is that method in use at the Whiting plant to-day?

A. Yes, sir.

Q. To what extent?

A. To convert the fuel oil that we don't have any sale for into lighter product; fuel and gas oil we don't have any sale for and contracts for, into lighter products, making them up into motor fuel, which is practically gasoline."

Furthermore, oil refiners all over the country are working on methods to convert every pound of gas oil into more valuable products. Facing facts, this means that if gas men are to continue the use of petroleum in carbureting water gas, they must resort to one of two alternatives:

1—Greatly increase the yield of gaseous hydrocarbons from a given amount of oil, or

2—Perfect methods of using the millions of barrels of fuel oil which to-day are considered unfit for carbureting water gas.

One often hears the statement that these so-called fuel oils cannot be used in carbureting water gas. What right does any one have to make this statement? Is it the result of scientific study and investigation, or is it the result of experiments carried out under the same old conditions which prevail in the use of Pennsylvania, Ohio or Indiana petroleum?

The purpose in emphasizing the gravity of the petroleum situation in connection with gas manufacture is not to destroy hope nor to disseminate pessimism for the future. On the contrary, I believe that as soon as the gas manufacturer faces facts as they are, and seriously attacks the problem, increased efficiency and economy will result with petroleum still of primary importance as a raw material. Never in the history of the world has so much oil been produced as is being produced to-day. It is estimated that Oklahoma<sup>2</sup> alone will mine 80,000,000, and California<sup>3</sup> will contribute 100,000,000 barrels. Never in the history of the United States has so much oil been in storage as to-day. We are not facing an oil famine. We are facing a famine of knowledge concerning the chemical behavior of inferior petroleum which will facilitate their substitution for higher grade petroleum.

If we accept the statement that the various so-called fuel oils cannot be used to carburet water gas, the necessity for scientific chemical research becomes more acute than ever. It means that carbureted water gas is entering a rapid decline, and is to be replaced by coal gas, by-product coke-oven gas, or some other process gas not developed to-day. The problems involving physical chemistry will not be eliminated. The phenomena of chemical change are involved in any process wherein a solid or liquid is converted into a gas of different constitution.

The machine becomes of vital importance when it favors or hinders optimum conditions for the end products desired. Aside

from operating costs, the relative merits of horizontal *vs.* inclined *vs.* vertical retorts depend entirely upon the influences of the retort's position on physical and chemical changes involved. The relative merits of any mechanical structure used in gas manufacture depend upon its influence on the chemical reactions which produce the ultimate end products. The vertical retort completely filled yields more tar and less gas than the practice of partially filling the vertical retort, simply because the vapors are subjected to different physical conditions which influence the degree of cracking and tend to bring about equilibria concordant therewith. This difference in end products, using the same type of machine, indicates the complexity of the chemical reactions of gas manufacture and the close relations which exist between prevailing conditions and end products obtained. Both coke-oven gas and retort gas are made by the application of heat to coal, yet the two gases vary considerably in their composition. Therefore, should we not look forward to a complete understanding of the composition of the raw materials, coal and petroleum, and the changes and mechanisms of the changes that take place in them under different physical conditions?

When pointing out the seriousness and the dimensions of the gas man's chemical problems, and when referring to the efforts and accomplishments of petroleum refiners, it would be unjust to overlook the excellent research work which has been started within the last three to five years. However, practically all of these investigations deal with coal. They are concerned with determining:

1—The composition of the coal.

2—The initial decomposition products.

3—The final decomposition products under varying temperatures and pressures.

4—The nature of the tars produced under varying temperatures and pressures.

I refer to the valuable work of Parr and Olin,<sup>4</sup> Burgess and Wheeler,<sup>5</sup> Ame and Fictet,<sup>6</sup> Fictet and Bouvier,<sup>4</sup> Rau and Lambris,<sup>4</sup> Vignon,<sup>5</sup> the Bureau of Mines, the United Gas Improvement Company, The Barrett Manufacturing Company, and numerous other investigators.

Much of this work may appear too academic, and questionable from a practical point of view. On the other hand, our industry progresses as the result of just such investigations. Regardless of whether a low-temperature process, for example, is valuable for direct application, the information obtained as to the constitution and chemical behavior of the coal is of utmost importance. The same information with respect to petroleum is equally essential. As a matter of fact, prior to the works above referred to, the extent of change that takes place in the destructive distillation of coal was a question. In other words, do the end products occur in coal as such, or are they formed in the operation? Does benzene occur in coal as benzene, or is it formed in the distillation? To-day these questions appear unnecessary and out of place. We now believe that benzene does not occur perceptibly in the original coal, nor does it occur in appreciable quantities in Eastern gas oils. The fact that it does occur considerably in both water-gas and coal-gas tars to-day, indicates conclusively that benzene is made in the course of the gas-making process. There has been a transformation, a chemical change. That this change is not a simple one can be observed from the investigations referred to. Further, it is found that when coal is distilled under a vacuum, very little benzene is formed. When the mechanism of benzene formation is fully understood, it will be a relatively simple

<sup>1</sup> Bull., Univ. of Illinois Engr. Expt. Sta., 1912; *Compt. rend.*, 137 (1913), 779.

<sup>2</sup> Trans. Chem. Soc., 1910, p. 1917; 1911, p. 649; 1914, p. 131.

<sup>3</sup> *Compt. rend.*, 187 (1913), 779.

<sup>4</sup> Jour. f. gasb., 66 (1913), 533, 557, 589.

<sup>5</sup> *Compt. rend.*, 1912, p. 1514.

<sup>1</sup> The Petroleum Gazette, July, 1914, p. 5.

<sup>2</sup> Oildom, Aug., 1914.

<sup>3</sup> Petroleum Review, 30, 599, 687, 717; 31, 3.

matter to increase or decrease the yield. Benzene is referred to purely as an illustration. The same reasoning applies to all tar, ammonia and cyanogen formation in connection with gas manufacture. If naphthalene is an undesirable product in gas manufacture, its appearance is not conclusive proof that its production cannot be avoided.

The variation in the tar obtained from different processes of coal, oil and coke-oven gases, is entirely due to variations in the prevailing physical conditions. It is a fact that these tars do differ, yet the initial materials used in the process of manufacture may be the same. With the reason for these differences fully understood, the optimum conditions for manufacture of both tar and gas will be understood and better realized. The tars which result from the destructive distillation of coal or oil, under different physical conditions, vary as widely as do the physical conditions under which they are made. In the course of a research carried out by Prof. M. C. Whitaker and the writer,<sup>1</sup> on the destructive distillation of petroleum, it was found that the tar made under greatly diminished pressure was radically different from that obtained by cracking the same oil under atmospheric or increased pressure. The vacuum tar was of much lighter specific gravity; it contained practically no free carbon; no naphthalene or anthracene settled out of the heavier distillates of the tar; the tar combined readily with 1.82 sp. gr. sulfuric acid. Tars resulting from cracking the same oil under increased pressure contained much free carbon; they were of considerably higher specific gravity; naphthalene and anthracene settled out of the distillates; they contained benzene; they would not combine readily with 1.82 sp. gr. sulfuric acid. The gas made under the two conditions was of equally different composition. The vacuum gas was a "dry" gas, in that it contained practically no benzene; on the other hand, it was high in ethylene homologues. The volume of uncombined hydrogen obtained under vacuum conditions was very much less than when the machine was under increased pressure. Further, there was practically no deposit of free carbon when working under a vacuum, whereas when the pressure on the machine was increased to three atmospheres, over fifty per cent, by weight, of the original oil was deposited as carbon.

principally with the machine under atmospheric pressure. Experiment shows that the moment we change the pressure, new results are obtained and a new series of experiments suggested. Certain it is that much remains to be done in the field of concentration, pressure and contact-surface changes. The application of various conditions for different periods of time still offers field for investigation.

I repeat that even if such investigations do not result in radically new processes, they will yield valuable information for a better understanding of, and improvement in, present-day processes. From a practical viewpoint, we may not as yet be able to see the advantages to be gained from the application of such scientific investigations, and, on the contrary, we may see disadvantages. However, this should not prevent our exploring the field. Industrial experience has again and again proven that the theory of to-day is the practice of to-morrow. In the absence of theoretical considerations, applied chemistry to-day would be in the medieval stages. As a typical example, the investigations of Haber<sup>1</sup> concerning the manufacture of ammonia from hydrogen and nitrogen were on a purely theoretical basis. From an initial yield less than 0.25 per cent, the process has been perfected to give a yield of well over 10 per cent of ammonia. From the idea of a man whose principal tools were theoretical chemistry, mathematics and physics, laboratory experiments developed into a process of commercial importance. The same laws maintain in the ammonia production of the gas plant that maintain in Haber's experimental and industrial apparatus.

The combination of nitrogen and carbon in the formation of cyanogen compounds is influenced by varying physical and chemical conditions just as surely as is the production of ammonia, whether from coal distillation or directly from the elements.

The application of physical chemistry, in mathematical terms, to industrial problems furnishes a means for quantitatively expressing yields and reactions taking place. I refer to the equilibrium relationship. Under some conditions it is highly important that the system reach a state of chemical equilibrium; under another condition, it would be fatal for the system to reach such equilibrium. Let us consider a few typical examples:

No.	Reactions	Heats of reaction	Volume changes	Partial pressures	$K_{eq}$	Approximate $K_{eq}$
1.....	$C + 2H_2 = CH_4$	+ 18900	2 to 1	$K = \frac{CH_4}{(H_2)^2}$	0.077	0.003
2.....	$2C + H_2 = C_2H_2$	58100	1 to 1	$K = \frac{C_2H_2}{H_2}$	$1.1 \times 10^{-13}$	$5.7 \times 10^{-10}$
3.....	$3C_2H_2 = C_6H_6$	- 163000	3 to 1	$K = \frac{C_6H_6}{(C_2H_2)^3}$	$9 \times 10^{13}$	$1.2 \times 10^{14}$
4.....	$C + H_2O = CO + H_2$	- 29300	1 to 2	$K = \frac{CO \times H_2}{H_2O}$	0.2	25
5.....	$CH_4 + H_2O = CO + 3H_2$	48200	2 to 4	$K = \frac{CO \times (H_2)^3}{CH_4 \times H_2O}$	0.06	3.46
6.....	$CO_2 + C = 2CO$	39650	1 to 2	$K = \frac{(CO)^2}{CO_2}$	0.1	59

Let us see how far the variables common to any gaseous chemical reactions have been investigated with respect to illuminating and heating gas. They are five in number:

- I—Temperature
- II—Pressure
- III—Concentration (mass action)
- IV—Duration (time)
- V—Contact surface

On the basis of combinations and permutations, it becomes evident that a great variety of manufacturing conditions can be obtained. Opinions naturally differ as to when a field has been properly and sufficiently investigated, and I, therefore, do not pretend to determine what proportion of the work remains to be done. It remains for each individual to form his own opinion. The field of temperature has been widely investigated, but

It becomes evident that for some reactions an elevation in temperature favors the preservation and formation of hydrocarbons, whereas for other reactions the same temperature is destructive. Considering equations 4 and 5, two of the most vital in present carbureted water-gas manufacture, one finds that a temperature of 900° C. is favorable to the CO and H<sub>2</sub> formation of both 4 and 5, but it is unfavorable to the methane preservation of 5. On the other hand, a temperature of 600° C. is unfavorable to the formation and preservation of CO and H<sub>2</sub>, but is decidedly more favorable than 900 to the hydrocarbon preservation of 5. At this lower temperature, however, the CO<sub>2</sub> of 6 predominates. From reaction 1 it becomes evident that methane is destroyed by high temperatures.

Numerical equilibrium expressions permit of quantitatively indicating the influence of three of the most important varia-

<sup>1</sup> THIS JOURNAL, 1914, pp. 383, 472

<sup>2</sup> Z. Elektrochem., 1913, p. 53.



bles of a gaseous reaction, *i. e.*, temperature, pressure and concentration. The value of the equilibrium constant increases or decreases with the temperature. Although pressure and concentration variations do not change the value of the equilibrium constant for a given temperature, the use of such equilibrium enables one to calculate the influence of changes in pressure or concentration for any given temperature. In reactions 1 and 3, referred to above, there is a decrease in the number of volumes due to the reaction; in reactions 4, 5 and 6 there is an increase in the number of volumes due to the reaction; in reaction 2 there is no change in the reacting volumes. According to the principle of Le Chatelier, pressure stimulates those reactions involving contraction, and vacuum stimulates those involving expansion. Pressure and vacuum are without influence on those reactions involving neither contraction nor expansion. For detailed consideration of the application of numerical equilibrium relationships, see articles by Whitaker and Rittman<sup>1</sup> and Rittman.<sup>2</sup> By a correlation of equilibrium conditions for the various reactions involved in gas manufacture, much help can be had in determining the course of experiments. Unfortunately, equilibrium relationships, as shown, do not indicate the speed of the reaction involved; they indicate the state of affairs after complete reaction has taken place and the system is balanced. Therefore, the information indicated by an equilibrium relationship is not complete in itself. No single reaction can be considered exclusively by itself. All the reactions in a process are vitally inter-related, though any single reaction, or set of reactions, may be extremely important as indicating a tendency.

The shape of the machine cannot change the equilibrium constant for any given reaction. It is easily possible to reach the same equilibrium in entirely different types of machines. The machine is vitally important in so far as its design provides conditions for a favorable or unfavorable equilibrium; or in so far as its design hastens or retards the system in reaching equilibrium. It would be an easy matter to expand indefinitely on the importance and practical application of equilibrium relationships with respect to gas manufacture, but it seems advisable to await further experimental evidence.

In conclusion, I would say that the application of physical chemistry to gas manufacture is stimulating, because gas manufacture is a chemical and chemical-engineering problem. It involves solids, liquids and gases with all the chemical and physical laws governing these three states of matter. The questions of energy and heat transformations determine profit or loss. Nowhere is the question of chemical equilibrium more important. Vapor pressure, surface tension, solubility, dissociation, diffusion, polymerization, catalysis, decomposition, specific heat, latent heats of reaction, speed of reaction constitute fundamentals in physical chemistry, and are all vital to the gas man. The five variables—temperature, pressure, concentration, duration, and contact surface—offer a flexibility which should permit equal flexibility in the character of the end products obtained. Complicated problems become elementary in the light of physical chemistry. The pendulum swings to the extreme where gas manufacture becomes primarily a problem involving theoretical and applied chemistry. Without its application the industry cannot develop. However, in view of the work which has recently been done and which is being done, we can feel that gas manufacture as a chemical problem is gradually coming into its own.

CHEMICAL SECTION OF PETROLEUM DIVISION  
BUREAU OF MINES  
PITTSBURGH, PA.

## THE BROADER APPLICATIONS OF CHEMISTRY BY THE MUNICIPALITY

By HERMANN W. MAHR

Received June 1, 1914

Chemistry has for the last decades been a valuable aid in securing the health and well-being of the dweller in American cities. Its fields of activity have been the inspection of foods, the all-important duty of controlling the quality of the water supply and the disposal of sewage. Beyond this, the science has only in rare instances been called upon for regular aid by the municipality.

In the meantime chemistry has been becoming an important factor in the industrial field. Chemists have improved processes and brought forth new products, many of which are finding wide use in civic housekeeping. The position now occupied by applied chemistry has led the far-seeing to herald the near future as the age of chemistry. With the advance in the industrial field have come additions to the knowledge and improvements in the methods of the science which now enable it to successfully attack special problems confronting our cities.

The chemists at present engaged in the all-important work of aiding in the conserving of the public health are often too well occupied with their duties to give time or attention to the technical problems which arise. Municipal engineers attempt to solve these questions, but are handicapped by a lack of knowledge of industrial chemistry and the ability to think chemically. These conditions give rise to opportunities for the chemist to aid the engineer and become his active co-worker. Members of the profession entering this work must necessarily be well acquainted with the processes of applied chemistry, and the methods of analysis and testing of industrial products, particularly the materials of engineering.

Our federal government has been a pioneer in this respect and its researches have redounded to its material advantage. It now has in its service well informed experts in many branches of industrial chemistry. The results of their investigations have been published and many of them are invaluable to the municipality. The latter should have in its service chemists able to apply the results of these governmental and of other technical investigations to the problems of the city.

A large portion of the expenditure of the municipal corporation is for the purchase of supplies. The value of the chemical laboratory in connection with this work has long been recognized. Some of our railroads were the first organizations to avail themselves of scientific supervision and inspection in this connection. The federal government has followed their lead and carried on the work through the Contracts Laboratory and similar testing stations in the large departments.

The first duty of the chemist concerned with the purchase of supplies is the inspection of materials delivered. Study of the various commodities and the framing of requirements is second only to the work of testing. Many proprietary compounds, of supposedly secret composition, with alleged wonderful properties, are urged on purchasing officials. On being subjected to chemical analysis these materials often prove to be composed of cheap ingredients for which a price greatly in excess of their value is asked.

The fuel bill of the municipality is probably the largest item of its budget for supplies. Competitive bidding, in accordance with well drawn specifications, has been universally adopted among large coal buyers as the best solution of the problem. In spite of its manifest advantages, city officials have hitherto been backward in putting a purchasing method of this nature into operation. The chemist can aid here greatly by studying the composition and heat value of the available coal supplies, drawing up requirements and testing shipments.

His labor in relation to fuel should, however, extend to over-seeing its proper and economical use. The importance of the

<sup>1</sup> THIS JOURNAL, 6 (1914), 383, 472.

<sup>2</sup> Jour. Soc. Chem. Ind., 1914, p. 626; THIS JOURNAL, 6 (1914), 684; and Metall. Chem. Eng., 1914, p. 475.

fuel question has, within recent years, assumed such proportions that chemists designated as fuel engineering chemists now make a specialty of the subject of fuel burning. A chemist, in municipal service, devoting himself to the wider application of chemistry, can make profitable studies of the methods of coal burning in schools and other public buildings. Wasteful grates may be found which require changes in the size of coal, and possibly expensive coals are burned where cheaper grades would adequately and economically furnish the required heat. Poor methods of stoking often allow opportunities for improvement with consequent saving.

Closely connected with the fuel question is that of obtaining proper boiler water. This part of municipal housekeeping is often entirely neglected, with a resulting increased consumption of fuel and decreased life of the heating or power apparatus. In some cases the man in charge is persuaded to buy a solution of sal soda and soda lye for a price many times in excess of its value. This mixture may or may not be adapted for use with the water in question. An examination of the water supply from the feed water standpoint will reveal the causes of trouble and enable the chemist to prescribe an inexpensive compound or the proper method of treatment.

There are many commodities purchased in large amounts whose composition is well enough known for them to be bought on specifications and subjected to test. One of the chief of these materials is soap, the cost of which is a considerable part of the amount expended for supplies. The federal government and railroads have long bought soap on well drawn requirements.

Within recent years the fact that "there is paper and papers" has been recognized. Large concerns are now paying attention to the quality of this material. The paper experts of the German government have made investigations and devised tests and methods of analysis for ascertaining the value of various papers. The uses of these methods have become known and are taken advantage of in the paper trade and by large users. Our municipalities are among the latter and can gain materially by scientifically scrutinizing paper supplies.

Rubber hose is an expensive necessity purchased in considerable amounts. On its quality and strength much depends. This has led insurance underwriters to require that hose for use in insured buildings be of the highest grade. Inspection of rubber requires it to be subjected to thorough chemical analysis and severe chemical tests. Cities should demand and make certain that hose for use by their fire departments and in public buildings is of the best quality.

Construction work of various kinds consumes a large portion of the civic bank credit. To obtain lasting structures and roads and prevent the use of inferior materials, the latter must be continually examined. Iron and steel should be subjected to chemical and microscopical analysis. Cements require chemical as well as physical tests. Results obtained by the chemist on a concrete containing one part cement to twelve of aggregate instead of one to six will often furnish grounds for civil or criminal action against an unscrupulous contractor. The water-proofing of concrete has occupied the attention of the engineer and technologist within the last few years. The importance of the subject has resulted in the appearance of many worthless water-proofing compounds whose nature and value can be best revealed by chemical analysis.

Paints and protective coatings have been investigated to good effect by our American chemists and their results have put this subject on a scientific basis. An understanding of these principles and knowledge of the properties of paints is necessary for the adequate protection of municipal buildings and structures.

Modern traffic conditions have been instrumental in bringing more of the products of applied chemistry into use by the city

than any other influence. The ingenuity and experience of the oil and coal tar chemists have been drawn upon to solve the problems arising from the use of the automobile. Various forms of pavement with permanent bituminous binders have come into wider use. The manufacture of new asphalts from oils in order to supplement the natural deposits owes its impetus to the demand thus created. Treatment of coal tar for use in tar macadam and as a semi-permanent surface binder has occupied the attention of the chemical technologist for the same reason. The lighter tar and oil products have also been studied and experimented with in the effort to produce dust preventatives. Treated wood block pavements are meeting with increased favor. Upon a knowledge of the properties of various treating media and thorough inspection and testing rests the success of these pavements and the comfort of those compelled to use them.

The city is called upon to apply the principles of preventative medicine on a large scale. Municipalities thus consume large amounts of antiseptics in their health departments. Disinfecting compounds flood the market. They, however, vary widely in ability to kill the various pathogenic organisms. The use of scientific tests for disinfecting value is not wide-spread in this country, but their introduction and use would result in a saving to the municipality with increased surety of the effect of treatments. Scientific inspection of disinfectants is a subject which also touches the household. It should be placed on the same plane as food inspection. Use of an inefficient antiseptic will often lead to more serious consequences than the consumption of a sophisticated food product.

Fire authorities have recently directed their energies toward the prevention of fires rather than their extinguishment. To make sufficient and effective rules governing the use and transportation of combustibles and enforce them requires the advice and service of members of the chemical profession. Within recent years the wide-spread establishment of garages has greatly increased sewer explosions. Chemical investigation is required to control this problem and place the blame at the proper source. The ultimate solution of the difficulty rests on chemists working in collaboration with the plumbing and sanitation experts of departments having authority over the erection of buildings.

Fire-proofing and requirements in regard to it also occupy the attention of the latter departments. We owe our modern fire-resisting materials largely to the work of technologists in the chemistry of ceramics. The national government has appreciated this fact and now maintains a department of the Bureau of Standards for testing and research in ceramics.

A problem which has been given much thought and attention by municipal officers is the disposal of refuse, especially garbage. No satisfactory or altogether profitable method of disposal has been evolved. The treatment of this waste has not as yet been well studied by the chemist. The field of work, being comparatively unexplored, offers commensurate reward to members of the profession who shall bend their energies to the work. The most apparent method of increasing the value of garbage is that of rendering available the nitrogen of tankage, which is now mostly in forms of little value for fertilization.

Legal investigations have in many important instances been aided by the services of chemists. The opportunities for their work in this connection are more varied and numerous than have been realized. This leads to the belief that the future will see a chemist with his microscope and laboratory attached to many police departments. His work will be not only the present well-known toxicological investigation, but he will devise and apply delicate methods to the interpretation of clues which have in the past been closed books. The service rendered by that new branch of chemistry, metallography, is one instance of this. Boiler explosions have been difficult to trace to their origin, but microscopical examinations will often reveal faults in the

heat treatment or structure of the metal which have caused disaster.

The foregoing outline suggests only a few of the possibilities for assistance that chemists may render our municipalities. An appreciation of the value of the science is necessary in the progressive civic official. More frequent attempts to throw the

light of chemical research on problems will lead to satisfactory and even gratifying results. Surely the science of Liebig, Perkin and Bunsen can render increased aid to our American cities.

STANDARD TESTING LABORATORY  
BOARD OF ESTIMATE AND APPORTIONMENT  
125-127 WORTH ST., NEW YORK

## CURRENT INDUSTRIAL NEWS

By M. L. HAMLIN

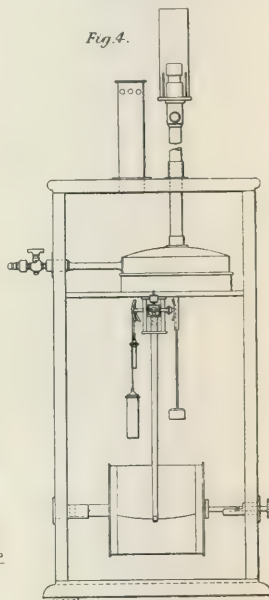
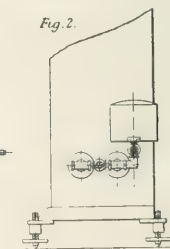
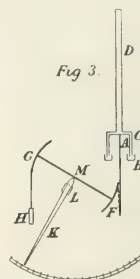
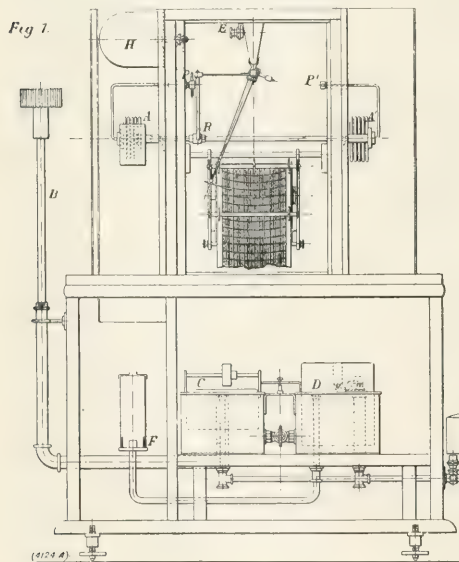
### INSTRUMENTS FOR TESTING GAS

At the Munich Gas Exhibition, Messrs. Alex. Wright and Co., London, showed instruments for testing gas, two of which—the caligraph and the gravitometer—are described in *Engineering* (London), 98 (1914), 362. The caligraph, which attracted much attention, is an instrument by means of which the calorific value of a gas is automatically recorded.

The principle on which it operates may be described as follows: A constant volume of gas is burnt. The heat from this combustion is caused to warm a certain quantity of air which then passes over one diaphragm of a differential thermometer, the other diaphragm being affected only by the room temperature. The indication of the differential thermometer, which is thus a measure

a tube, B, at the top of which it is consumed by a small flame. This is prevented, by means of a special burner, from heating the gas in the tube. Any variation in specific gravity of the gas will obviously cause a difference in weight of the column of gas in the tube B, and will thus alter the pressure in the left-hand bell C. This alteration in pressure will cause the bells to move and actuate the gas-admission valve. In this way a constant supply of gas to the burner F is assured, no matter what the density of the gas may be.

The differential thermometer consists of two metal diaphragm boxes, A and A', filled with air, one at each end of a glass rod, R. Any movement of this rod is recorded, by means of a pen actuated by link-work, on a chart wrapped round a revolving



of the heat given off from the gas on combustion, is marked by means of a pen, actuated by suitable link-work, on a chart passing over a clock-drum.

Referring to Figs. 1 and 2, the constant consumption of gas is obtained by means of a governor consisting of two bells, C and D, which are connected and swing on needle-points. The gas passes through a dry governor (to take up any sudden variation in pressure) into the right-hand bell D by means of a valve. The extent of opening of this valve is determined by the position of the bells. The gas passes out of the bell D through a gold nipple of standard size to the burner F, where it is consumed. At the same time the gas can also pass from the dry governor into the left-hand bell C by means of a by-pass cock. This gas passes out of the bell C through

drum, which is driven by clock-work. As the temperatures of the diaphragms vary, the air in them will expand or contract, thus causing a movement of the glass rod, and as the right-hand diaphragm is affected by the room temperature only, while the left-hand one is affected by the heat from the flame as well as by that from the room temperature, the movement of the rod, being the difference of the two effects, is proportional to the heat obtained from the combustion of the gas at F. It will be observed that any alteration in temperature and in atmospheric pressure will affect the air being heated in the same way as the gas burnt, thus automatically compensating for any change in the number of the tables of constants which are used in connection with the instrument.

The essential principle of the gravitometer is illustrated in



Figs. 3 and 4. The instrument is essentially a gas-balance, in which the specific gravity of the gas under test is compared with that of the surrounding air. This is accomplished differentially, the weight of a column of gas and the weight of an equal column of air being arranged to act on opposite sides of what is virtually a scale-pan, and the difference in weight registered.

The bell of the gravitometer may be considered as a scale-pan on which the pressure below is due to the pressure of the atmosphere on the lower surface, and the pressure above to the pressure of a column of gas added to the pressure of the atmosphere at the top of that column, the aggregate being less, in the case of coal-gas, than that of the atmospheric pressure below the bell. Gas is always passing up the tube to supply the burner at the top, and under these conditions is under absolutely the same conditions of temperature and pressure as that of the surrounding air. It will thus be seen that the pointer of the gravitometer indicates the weight of that column of gas of a height equal to that of the tube. For example, with a bell of 6 in. diameter and a height of tube of 30 in., the gas of, say, 0.9 specific gravity is 15.9 grams.

The pressure or weight on the top of the bell is in direct proportion to the specific gravity of the gas in the tube, and is, in addition, proportional to the height of the tube. Thus, if the tube were 60 in. in height instead of 30 in., the pressure on the bell, due to the weight of the gas, would be 30.38 grams, and the movement of the pointer across the scale would be twice that in the case of the 30-in. tube. Mechanical considerations constitute the only reason for not using a longer scale; indeed, by employing tubes of sufficient height, it is possible to measure specific gravity to any required degree of accuracy.

Referring to Fig. 3, which shows diagrammatically the action of the gravitometer, A represents a light aluminium bell, sealed in oil contained in the annular tank B. The bell is covered by a shell, C, which is not in contact with it. The top of the shell carries a tube, D. The bell is free to move up and down, and is carried by a vertical support connected to the end of the balance-beam G by a hanging chain. The other end of the beam carries a hanging weight, H. The chains connected to both H and A pass over circular arcs. A pointer, K, and a gravity-control weight, L, complete the essentials of the instrument. On a stream of gas passing slowly over the bell A and up the tube D, the pressure on the top of the bell is diminished and the pointer K swings into a new position of equilibrium. The scale over which the pointer moves is graduated to read or to record specific gravity directly.

### THE IMPERMEABILITY OF CONCRETE

In a paper recently read before the Western Society of Engineers and quoted in *Engineering* (London), 98 (1914), 483, Professor M. O. Withey described the results of a series of tests on the permeability of concrete, which have been made at the University of Wisconsin. The materials used were Portland cement, sand ranging in weight from 104.5 lbs. to 112.2 lbs. per cu. ft., and gravel weighing from 107.3 lbs. to 190.3 lbs. per cu. ft. Eighty-eight of the test-pieces were made with a 1 :  $1\frac{1}{2}$  : 3 mixture by volume, and sixty-seven with a 1 : 2 : 4 mixture, and there were ninety-eight specimens proportioned with 1 part by weight of concrete to 9 parts by weight of aggregate. None of the concretes proved absolutely water-tight in the sense that they would not absorb water, but most were so impervious that there was no visible evidence of flow. The signs of dampness on the bottom of the specimens increased with increasing humidity of the atmosphere. With mixture of 1 part of cement to 7 parts of aggregate the average rate of flow during a period of fifty hours was under 0.001 gal. per sq. ft. per hr., when the pressure was 40 lbs. per sq. in. With the 1 to 9 mixtures, prac-

tically water-tight concrete could, it was found, be obtained by suitably grading the sand and gravel. Richer mixtures, such as the 1 :  $1\frac{1}{2}$  : 3, proved very impervious, but Professor Withey remarks that such rich mixtures show considerable volume changes when alternately wetted and dried. To secure impermeability great care is needed in mixing the concrete, especially when the proportion of cement is small. If mixed too dry, the concrete cannot be properly compacted. The best results were obtained by mixing the materials dry for  $\frac{1}{4}$  to  $\frac{1}{2}$  min., and then continuing the process after adding the water for  $1\frac{1}{2}$  to 2 min. with 1 to 9 concrete, or for 1 min. with the rich 1 :  $1\frac{1}{2}$  : 3 mixture. Proper curing of the concrete greatly adds to its impermeability. Premature drying destroys the imperviousness of the lean mixture, seriously impairs that of the 1 : 2 : 4 mixture, and appreciably diminishes the water-tightness of the rich mixture. Thus, thin sections of 6 in. to 8 in. in thickness should be, he concludes, kept damp for one month for lean mixtures, or two weeks for a rich one.

*Engineering* also quotes (vol. cit., 446) from *Science Spectacular*, a publication of the Society of Arts of the Massachusetts Institute of Technology, some particulars of an interesting series of experiments now being carried out by the Aberthaw Construction Company in order to disprove the theory that the combined effects of sea-water and frost rapidly destroy concrete structures.

With this object in view, twenty-four concrete columns, 16 ft. long, 16 in. square, and reinforced with bars near the corners, were constructed in January, 1909, and immersed in the water at Boston Navy Yard. They were suspended in such a manner that at high tide the water reaches nearly to the top of the column, and falls at low tide nearly to the bottom. In cold weather the columns are thus alternately thawed and frozen as the tide rises and falls. The columns were made with various qualities of concrete mixed dry, plastic, and very wet. Different qualities of cement were used, and the effects of waterproofing materials, clay, and other additions to the concrete are being studied. One of the columns was mixed with salt water, but this was unfortunately lost in handling.

No final conclusions are, of course, possible yet; many years must, in fact, elapse before it will be possible to say which kind of concrete is most permanent. When examined in December last many of the specimens were practically unaffected, but others were badly eroded. As might be expected, the best results were given by the specimens richest in cement and mixed wet. For instance, of two columns made with 1 part of cement to 1 of sand and 2 of stone, the one mixed dry was badly eroded over the whole of its length; whereas the other, which was mixed very wet, was only slightly pitted. Again, of two specimens made with slag cement in the ratios of 1 : 1 : 2 and 1 : 3 : 6, respectively, and both mixed wet, the former was in excellent condition, with only very slight pitting, while in the latter all the corners had gone and the reinforcement was exposed in places. The part of this specimen which was continuously immersed was, however, in very fair condition. The experiments are being continued, and doubtless some very interesting results will be obtained in time.

### PUTTING ELECTROTYPING INDUSTRY ON MORE SCIENTIFIC BASIS

At a meeting in New York on October 7, 1914, the International Association of Electrotypers appointed a committee to cooperate with the Bureau of Standards in a study of the conditions in the electrotyping industry, with a view to assisting in placing it upon a more scientific basis. A preliminary circular giving simple directions for testing and adjusting the density and the acidity of the copper electrotyping solutions has been prepared, and may be obtained upon request from the Bureau of Standards, Washington, D. C.

# THE BALANCE OF TRADE IN CHEMICALS BETWEEN THE UNITED STATES AND GERMANY IN 1913

In an article in THIS JOURNAL, 6 (1914), 274, by B. C. Hesse, it was shown that the tonnage of chemicals exported from this country to Germany was considerably in excess of that imported from Germany, the difference in our favor being 404,295,500 kg., or in round numbers, 890,000,000 lbs.

Recently the values of the separate items, listed according to the German official classification, were published [Chem. Ztg., 38 (1914), 962], and it became possible to estimate the value of the trade balance as follows: the total value of the German

import or export taken from the above mentioned German table was multiplied by the percentage of weight of total German import or export originating in or sent to the United States, and this value changed to dollars. These results together with Hesse's figures are given in Table I following. Table II summarizes Table I and shows also the balance in each class in favor of one country or the other. The total balance is in favor of the United States and amounts to over \$95,000,000.

This balance is not strictly comparable with the smaller one of \$21,000,000 calculated for 1904 by Hesse in THIS JOURNAL, 6 (1914), 2, because the later list is much more extensive, con-

TABLE I—CHEMICAL TRADE OF THE UNITED STATES WITH GERMANY—1913

Official sub-class	UNITS OF 100 KG. VALUE (\$1000) IN = 0.1 LONG TON \$1000 UNITS				Official sub-class	UNITS OF 100 KG. VALUE (\$1000) IN = 0.1 LONG TON \$1000 UNITS			
	U. S. to Germany	U. S. from Germany	U. S. to Germany	U. S. from Germany		U. S. to Germany	U. S. from Germany	U. S. to Germany	U. S. from Germany
I—MALT, OIL FRUITS, INDUSTRIAL PLANTS, FRUITS AND PLANT JUICES									
30 Hops.....		11,119		952	239a Mineral lubricants.....	1,024,673	8,415	4,460	61
32 Madder, quercitron and other dye plants.....	3,403		29		239b Crude petroleum, etc.....	1,619			3
60a Opium.....		165		168	239c Heavy benzine, patent-turpentine.....	18,194		97	
II—INDUSTRIAL OR MEDICINAL VEGETABLE PRODUCTS					239d Gas oil.....	55,468		656	
72c Lichens, herbs, berries, leaves and buds.....	4,567	5,499	114	200	239e Refined petroleum.....	5,747,587		12,690	
73 Vegetable wax.....		1		030	239f Crude benzine.....	418,159		2,220	
89 Sawdust and excelsior.....		27,671		48	239g Benzine, ligroin, misc. light distillates.....	15,712		120	
III—TANNING EXTRACTS					239h Miscellaneous crude mineral oils.....	18,746		49	
384c Miscellaneous tanning extracts.....	213		16		250i Crude hard paraffin.....	87,028		1,231	
IV—RESINS, LACQUER AND VARNISHES, ADHESIVES					251 Soft paraffin.....	100		1	
97a Turpentine resin.....	770,100	2,619	4,585	17	240a Asphalt and asphaltic minerals.....	68,116		72	
97c Damar; hard and soft gums and resins.....	11,168	560	300	20	241 Crude ozokerite, etc.....	11,443		135	
97f Shellac.....		1,179		45	249 Refined ozokerite, etc.....	52	5,214	2	129
97f Gum acacia, Bassora gum, etc.....		1,027		22	243a Pitch.....		8,078		104
97g Gum tragacanth.....		625		40	XIV—COAL-TAR OILS AND PRODUCTS				
342 Alcohol and shellac varnishes.....	84		2		245b Anthracene and heavy oils.....	159,944		256	
343 Miscellaneous and coach varnishes.....	4,447	1,975	71	55	246a Naphthalene.....	7,242		18	
345 Putty and miscellaneous putties.....	829		14		246c Phenol, crude or refined.....	12,098		230	
346 Asbestos paint and putties.....	668		7		246c Cresol.....		2,152		476
V—CAOUTCHOUC AND CAMPHOR					246c Anilin oil and salt.....		24,282		149
98a Caoutchouc, crude or refined.....	364	20,019	53	2,582	246f Naphthal and naphthylamin.....		6,379		247
98b Gutta percha, crude or refined.....	272	911	33	76	246g Anthraquinone, nitrobenzol, toluidin, resorcin, phthalic acid, etc.....		9,651		242
98d Rubber scrap and waste.....	3,145	13,741	24	229	XV—WAXES				
VI—ANIMAL AND VEGETABLE FATS AND OILS					247a Beeswax.....		1,116		82
126a Hog lard.....	1,011,812		26,700		XVI—SOAP AND FAT PRODUCTS				
126b Oleomargarine.....	196,328		4,880		254 Soft and textile soaps; Turkey-red oil, etc.....				
126c Goosefat, beef-marrow, etc.....	1,091		21		256 Soap in cakes, powder, liquid, etc.....		6,208		59
128a Prime beef tallow.....	85,998		2,171		257a Crude glycerin.....		5,037		128
129 Beef and mutton tallow.....	35,498		579		257b Refined glycerin.....	10,285		147	
130 Bone-fat, fat-waste, stearin-fat.....	16,809	37,005	208	335	258 Vaseline and lanolin.....	10,285		147	
131a Fish oils.....	6,417		72		260 Lubricants made of fats or oils.....	68,384		617	
166d Peanut oil.....		16,058		323	262 Shoe polish.....	243		14	
166a Cotton-seed oil.....	99,950		1,550		264 Stearin, paraffin materials.....	395		16	
166b Beechnut, bone, corn, poppy, sunflower, etc., oils.....	19,127		286		XVII—CHEMICAL AND PHARMACEUTICAL PRODUCTS				
168 Cocoa-butter.....		4,798		316	266 Alkali and other metals.....		411		18
170 Cotton-stearin.....	3,335		55		270 Sulfur and Spence metal.....	71,535		187	
171c Palm oil.....		136,684		280	276 Oxalic acid and potassium oxalate.....		26,066		319
171b Coconut oil.....		2,150		39	277 Acetic anhydride.....		832		13
172 Oleic acid, olein, etc.....	5,875		84		278 Lactic acid and lactates.....		2,040		31
205b Edible vegetable fats.....		345		8	279a Tartaric acid.....		1,235		2
VII—ANIMAL PRODUCTS					280c Crude salts of 12-15 per cent K <sub>2</sub> O.....	5,412,614		3,213	
142 Spermaceti.....	135		6		280d Salts of more than 15-19.9 per cent K <sub>2</sub> O.....	412,926		338	
150f Bones and hoofs.....		10,821		30	280e Fertilizer salts and fertilizers with 38 per cent K <sub>2</sub> O.....		2,168,204		3,695
VIII—STARCH AND SUGAR					280f "Abrum" and miscellaneous salts.....		131,626		64
173c Potato starch, wet, dry or ground.....		15,222		109	283 Barium chloride.....		13,434		32
173a Corn, wheat and other starches.....	5,833		58		289a Caustic potash, solution or solid.....		38,173		192
174 Starch-gums (dextrin), roasted starch and gluten.....		19,460		174	290 Potassium carbonate.....		78,339		682
176c Beet sugar, all forms, refined.....		22,112		716	292 Bleaching powder, barium and hydrogen peroxide, etc.....		82,634		290
176f Beet sugar, raw.....		101,504		492	295a Potassium sulfate.....		536,741		2,287
177a Glucose, etc.....	5,217		31		295b Potassium phosphate.....		13		300
IX—ALCOHOL, ACETIC ACID, YEAST, MINERAL WATERS					298a Alums, aluminum acetate, alumina, etc.....		7,605		38
190 Mineral waters, inclusive of bottles.....		20,419		103	299 Chromium oxide and copper alums.....		4,794		53
X—MINERAL AND FOSSIL RAW MATERIALS					304b Barium nitrate.....		6,078		48
223a Clay (potter's pipe, fire, etc.).....		223,922		70	306 Potassium manganate and permanganate.....		3,978		65
224d Graphite, crude, ground and washed.....	10,763		63		308a Potassium and sodium ferro- and ferricyanide.....		10,179		248
225a Pumice and tripoli, crude, ground and washed.....		1,761		9	308b Potassium and sodium cyanide.....		25,619		845
225c Mineral abrasives polishes and rouges.....		6,675		57	309a Acetic acid of lime.....	203,643		1,162	
227b Magnetite.....		10,856		27	312 Tartar emetic and other antimony products.....		1,284		51
227d Phosphate rock and other mineral phosphates.....	4,212,124		4,970		314 Strontium carbonate, oxide and chloride.....		2,077		62
230a Portland, etc., cement.....		104,423		89	315 Zinc chloride and other zinc salts.....		903		5
231b Asbestos, crude and in fibers.....	48,151		422		316b Carbides of aluminum, silicon, etc.....	18,261		489	695
231c Mica.....	575		442	75	317a Sulfate of ammonia.....		56,296		339
232a Heavy spar and celestine.....		350,196		30	317b Arsenious acid.....		10,947		139
236a Boronatrocalcite, etc.....		2,088		111	317c Epsom salts.....		46,816		81
236c Miscellaneous earths, e. g., Fuller's earth, etc.....		41,987		30	317d Chlorides of magnesium and calcium.....		68,771		82
XI—ORES, IRON AND SLAGS					317f Potassium chloride.....	2,611,137		9,220	
237a Antimony ores and matte.....		210		2	317f Potassium magnesium sulfate.....	222,978		509	
237f Gold ores.....		4		506	317k Lime-nitrogen, nitro-lime and other fertilizers.....		231,976		635
237g Copper ores and cuprous cinder.....	2,501	25,854		9	317m Nitrites.....		4		050
237h Manganese ores.....		4,610		8	317n Salicylic acid and salicylates; saltonin; benzoic acid and benzoates.....		2,672		229
237i Zinc ores.....	132,088		366		317o Ammonium chloride.....		19,127		232
237j Uranium, molybdenum and other miscellaneous ores.....		6,731		239	317s Sodium sulfhydrate, lead compounds and misc. metalloids, acids, salts.....	32,939	88,971	482	1,602
XII—FOSSIL FUELS									
238d Coke.....		185,492		114					
238a Vegetable charcoal.....		6,664		11					
(a) M 1.00 = \$0.238.									

(a) M 1.00 = \$0.238.

TABLE I—CHEMICAL TRADE OF THE UNITED STATES WITH GERMANY—1913—(Continued)



## NOTES AND CORRESPONDENCE

### STRONTIUM IN THE BEET SUGAR INDUSTRY

*Editor of the Journal of Industrial and Engineering Chemistry:*

No more interesting commentary on the trade that is bound to accrue to American chemical manufacturers through the failure of continental suppliers to meet the demands of the American market, can be made than the foundation of a new industry directly traceable to the present chaos existing in the industrial world abroad. This is the manufacture of various strontium salts, which heretofore have been produced solely on the Continent. Within the past month over 300 tons of strontia ore (celestite, strontium sulfate) have entered the United States at the port of Philadelphia through the agents of the only commercially productive deposit in the world. It has been estimated that this quantity will no more than meet the pressing demands of certain consumers who, prior to the war, imported the refined salts chiefly in the form of strontium nitrate at figures entirely out of keeping with the known cost of production. Prior to August 1st of this year, the refined nitrate was offered in commercial lots at 8 cents per lb., but since the above date, the price of the salt has advanced 200 per cent. So far as statistics show, this is the largest quantity of strontium ore ever brought into the United States. Scarcity of raw material and the higher labor costs in this country have evidently deterred manufacturers from entering the world's market as producers of strontium compounds. For the American manufacturer to meet his foreign competitor on the same footing, it was necessary to secure a cheap and reliable source of supply, but now, with raw material at a price approximating that paid by foreign manufacturers, we shall be able to not only meet the demands of the domestic market but, in all probability, export a considerable portion of our total production.

The commercial demands for strontium nitrate are not so diversified as for certain other chemical products, but the total annual consumption in the United States seems to fully warrant the American manufacturer entering upon this new field with the confidence that once his market is established, he need no longer fear ruinous competition from the foreign producer.

The principal salts of strontium that appear on the commercial market are, in the order of their importance: strontium hydroxide, strontium nitrate and strontium chloride. Of the above salts, however, the nitrate is the only one that has been imported in large quantities, but the world consumption of this salt is very small in comparison to that of the hydroxide, which is used in the refining of beet sugar molasses. So far as is known, the major portion of the nitrate imported annually is consumed in the manufacture of railway signals or Coston lights, and the manufacture of so-called red fire used extensively by the pyrotechnists.

For reasons best known to the continental sugar refiners, the price of the hydrate has never been within the reach of our domestic consumers, but inquiries made among large beet sugar refiners in this country indicate that there would be a very large consumption of the compound, provided a stable source of supply could be secured.

The conversion of celestite, or strontium sulfate, into soluble strontium compounds, is effected through the reduction of this salt by heating with carbon in rotary furnaces, thus producing the soluble strontium sulfide, from which the hydroxide or nitrate can be readily prepared with suitable reagents.

In the desaccharization of beet sugar molasses, containing generally some 40 to 50 per cent of sugar, which owing to the presence of small quantities of certain inorganic salts will not crystallize out, there are at present three methods employed to

effect desugarization: 1—Strontia process, 2—Osmosis process, 3—Lime process.

Of these three, the most effective, efficient and economical is the strontia or Scheibler process. This depends on the reaction that occurs when an excess of strontium hydroxide is added to a dilute sugar solution at a temperature exceeding 100° C. The work is carried out in suitable boilers provided with steam coils and agitators, a 20 per cent to 25 per cent solution of the hydroxide being first heated and the molasses added in amount equal to about one-third that of the strontium solution. The liquid is then rapidly agitated, the temperature being kept above 100° C., when there occurs a granular, sandy precipitate of strontium disacrate. This is rapidly filtered and washed with a boiling 10 per cent solution of strontium hydroxide, the disacrate being insoluble in hot solutions. After the precipitate has been thoroughly washed, it is dissolved in a cold solution of the hydroxide and allowed to stand for several days in crystallizing tanks. At the end of this time, about 50 per cent of the hydrate separates in crystalline form and the saccharine solution is decanted and the crystalline residue centrifuged to free it from the solution. Carbon dioxide is then passed through the sugar solution, thus causing a precipitation of the balance of the strontium as the carbonate. This compound is reconverted into the hydroxide by calcining and dissolving the resultant oxide in water. The ratio of the total strontium hydroxide required for the precipitation of sugar in the beet molasses is approximately  $2\frac{1}{2} : 1$ . A remarkably pure sugar solution is obtained by the strontia process, so that the sugar, after crystallization, can be placed directly on the market without further refining.

At the present time the methods in vogue in this country are the osmosis and lime or Steffen process. The former is rather slow and necessitates the handling of the same solution a number of times. The lime process requires special cooling apparatus, as the temperature of the sugar solution must be kept below 15° C. during the precipitation of the tricalcium succrate, which is readily soluble at a higher temperature. There are numerous other minor objections to both of these processes, so that although the initial cost of the strontia process may be more than either of these, it can be readily seen that it is much more effective and rapid.

In connection with the regeneration of strontium hydrate, an American patent has just been issued describing a process for the rapid conversion of strontium carbonate into the oxide through the use of certain fluxes such as fluorspar, soda ash, etc. In the past, some difficulty has been experienced in treating the impure strontium carbonate precipitated from sugar solutions, owing to its being contaminated with lime, silica and certain organic substances.

Statistics show that Germany desaccharizes annually about 100,000 tons of beet sugar molasses. As nearly all the continental beet molasses is desugarized by the strontia process, this would indicate that over 100,000 tons of strontium hydroxide are employed in Germany alone. It must be remembered, however, that this does not indicate the annual consumption, which is probably very much less than this figure, owing to the fact that the strontium compounds are nearly all recovered by various regenerative processes, so that the percentage of loss is rather small.

The American beet sugar industry is still in its infancy compared to that of Europe. During the last few years the production fluctuated between 600,000 and 700,000 tons annually, all of which was for domestic consumption. It would not be safe to predict at the present time just what increase in this annual production the introduction of the strontia process would

effect, but with the coöperation of the American chemist, the process is likely to play an important part in the American technology of beet sugar.

FOOTE MINERAL CO., PHILADELPHIA  
November 14, 1914

H. C. MEYER

## THE EFFECT OF STEAM UPON MAGNESITE BRICK OR CALCINED MAGNESITE

*Editor of the Journal of Industrial and Engineering Chemistry:*

Carbonate of magnesia or magnesite is found chiefly in Greece, Austria-Hungary, Africa, India, and in California in the United States. The deposits of Greece and California are of the white massive character and as a rule of very pure quality. They are not as suitable for refractory purposes in metallurgical processes as the Austro-Hungarian magnesite, on account of composition and high cost of preparation. The white magnesites are used principally in paper manufacture, in caustic form as flooring cement, and for the manufacture of carbonic acid gas, the carbonate as mined containing approximately 50 per cent of  $\text{CO}_2$ , which may be driven off at a comparatively low temperature. A few refractory brick are made from white magnesite, but difficulties of manufacture and high cost render the demand very slight.

It is with the Austro-Hungarian magnesite that the users of magnesite in this country are most interested. The material occurs in a crystalline formation and is gray in color with tinges of brown. In comparison with the white magnesite it differs in composition and formation. The chemical composition is the most important difference. Comparative analyses of the two kinds of magnesite, calcined, are as follows:

	Austro-Hungarian	White
Silica ( $\text{SiO}_2$ )	2.75	2.50
Alumina ( $\text{Al}_2\text{O}_3$ )	0.50	0.25
Iron oxide ( $\text{Fe}_2\text{O}_3$ )	7.00	1.00
Lime ( $\text{CaO}$ )	2.50	2.25
Magnesia ( $\text{MgO}$ )	87.00	93.00
Loss on ignition	0.75	1.00

The impurities in the Austro-Hungarian render it less refractory, and it will frit more readily at operating temperatures, which is a very important property, especially in open hearth steel practice in building the bottom and repairing the slag line. In the calcined form, for commercial uses, Austro-Hungarian magnesite has a rich brown color and white magnesite is either white or a very light brown, depending on the thoroughness of calcination.

The chief uses of magnesite brick are in open hearth steel furnaces, copper converters, reverberatories and settlers, and electric furnaces. Their use is spreading considerably where strong basic slags, mill cinder and strongly metallic slags are encountered, such as the bottoms of forging, heating and welding furnaces.

It is an interesting fact, and one of importance to all users of magnesite, that when subjected to the action of steam, magnesite in calcined form, or even the most thoroughly burned brick, will hydrate, similarly to the action of calcined lime when water is added. This hydration takes place to equal degree in all brands of magnesite brick made in the United States or Europe. The effect of the hydration is disintegration to an almost impalpable powder. It does not seem to bear any relation to the content of lime or other impurities, as the tests showed the same results for the Austro-Hungarian as for the white or very pure Grecian magnesite.

Tests were conducted by placing brick in a steam-tight cylinder and subjecting to steam at 100 lbs. pressure for a period of two hours, all brick tested showing hydration to the same degree, though it is reasonable to conclude that the action would be somewhat retarded under lower pressure or less severe conditions.

Difficulties of this nature have been experienced in open hearth furnace bottoms by laying the brick and magnesite bottom over a bed of refractory materials mixed with water. Upon heating up, steam is formed and the bottom may be very badly damaged by hydration of the magnesite.

This fact, which has not been well established until recently, no doubt accounts for a number of similar troubles which have occurred in years past. It also explains cases of disintegration of burned magnesite brick which have been in contact with steam leaking from coils or steam-heated floors used in manufacturing magnesite brick. It should be made a matter of common knowledge, therefore, so that users of magnesite will be able to guard against trouble of this kind, especially during the initial heating period.

HARBISON-WALKER REFRACTORIES CO.  
PITTSBURGH, September 15, 1914

R. H. YOUNGMAN

## CONVERSION TABLE FOR GLUES

In connection with the use of the Weinlagen Glue Hydrometer, which reads percentage by weight of air-dry glue, it is necessary to calculate the number of pounds of glue in a gallon of the dry product, as well as to determine the capacity of tanks and other glue containers in terms of air-dry or bone-dry glue. In determining the following values by experiment, a hide glue was used and the methods employed were of a degree of accuracy commensurate with technical use. The percentages selected are those generally dealt with in commercial glues.

Per cent air-dry glue (Hydrometer)	Corresponding percentage bone-dry glue	LBS. PER GALLON WHEN Air-dry	Bone-dry
0.0	0.000	8.3360	8.3360
0.5	0.424	8.3550	8.3570
1.0	0.848	8.3650	8.3690
1.5	1.270	8.3750	8.3810
2.0	1.690	8.3860	8.3930
2.5	2.100	8.3970	8.4060
3.0	2.550	8.4080	8.4190
3.5	2.970	8.4190	8.4320
4.0	3.390	8.4300	8.4440
4.5	3.820	8.4410	8.4570
5.0	4.240	8.4515	8.4700
5.5	4.660	8.4625	8.4820
6.0	5.080	8.4730	8.4945
6.5	5.520	8.4840	8.5080
7.0	5.940	8.4950	8.5210
7.5	6.360	8.5050	8.5330
8.0	6.780	8.5160	8.5460
8.5	7.210	8.5270	8.5590
9.0	7.620	8.5380	8.5715
9.5	8.060	8.5480	8.5840
10.0	8.490	8.5590	8.5970
10.5	8.900	8.5700	8.6100
11.0	9.340	8.5800	8.6225
11.5	9.750	8.5910	8.6340
12.0	10.180	8.6015	8.6460
12.5	10.600	8.6130	8.6600
13.0	11.020	8.6230	8.6715
13.5	11.450	8.6340	8.6840
14.0	11.870	8.6450	8.6970
14.5	12.300	8.6550	8.7100
15.0	12.720	8.6660	8.7225
15.5	13.150	8.6770	8.7360
16.0	13.570	8.6880	8.7490
16.5	14.000	8.6990	8.7610
17.0	14.410	8.7090	8.7740
17.5	14.850	8.7200	8.7870
18.0	15.270	8.7310	8.8000
18.5	15.700	8.7420	8.8130
19.0	16.100	8.7530	8.8260
19.5	16.550	8.7640	8.8390
20.0	16.970	8.7740	8.8520

BAEDER, ADAMSON & CO.  
PHILADELPHIA, August 1, 1914

ISMAR GINSBERG

## CAP FOR BUNSEN BURNER USED WITH NATURAL GAS

*Editor of the Journal of Industrial and Engineering Chemistry:*

Special burners adapted for natural gas are already in much use. But Bunsen burner and other modifications of this can be rendered serviceable for natural gas by providing caps made of ordinary wire gauze, say about 22 mesh. A cap made of wire gauze and put on a Bunsen burner or this type of burner gives a steady flame, not extinguishable even by a strong air draught. Such a cap can easily be made by pressing a piece of

wire gauze down over the aperture of an iron tube. One square inch wire gauze, 22 mesh, will answer the purpose. The flame of the wire gauze capped burner can be regulated very easily by the air regulator.

NATIONAL CARBON CO.  
CLEVELAND, OHIO, June 1, 1914

GREGORY TOROSSIAN

## A SHAKER FOR THE MECHANICAL ANALYSIS OF SOILS— NOTE

*Editor of the Journal of Industrial and Engineering Chemistry:*

IN THIS JOURNAL, 6, 517, Mr. C. C. Fletcher takes exception to my claim that my Soil Shaker is better than that used by the Bureau of Soils at Washington. I should like to consider his objections and further substantiate my claim.

I. NUMBER OF BOTTLES—It is true that the Bureau machine carries 48 bottles, while mine carries only 16. But the comparison becomes fairer by considering the power required to run the two machines. In the description of the Bureau machine<sup>1</sup> it is stated that "the machine is driven by an ordinary stock  $\frac{1}{4}$  H. P. motor." Determinations recently made on my machine by the Department of Mechanical Engineering of Yale University, show that 0.000766 H. P. is required to run it at the prescribed rate and loaded to full capacity. We then have a comparison of powers as follows: 0.25 vs. 0.000766—a ratio of 1 to 326+. Even if only one-tenth of the power of the motor were really used to operate the Bureau machine, that same amount of power would be sufficient to operate more than 30 of my machines at once, with a total carrying capacity of 480 bottles. One should bear in mind, also, the fact that my machine is strictly "home-made." If it were nicely constructed, mounted on bearings, etc., the efficiency would be even more striking.

II. SPEED—It is true that if the wheel were turned very rapidly there would be centrifugal effects. But it is expressly stated in my article that the wheel should *not* be run rapidly. Surely, the mechanical difficulties of running a wheel slowly instead of rapidly are not insurmountable! And indeed, the slower the wheel is turned the less energy is required. The "merely pouring" of the contents of the bottle from one end to the other, consequent upon slow turning of the wheel, is a distinct advantage over hitting the soil particles swiftly together by a sudden jerking motion.

III. ELEMENT OF TIME—Mr. Fletcher explains the 7 hours required by the Bureau machine by saying "in some rare instances as long a time as this has been found necessary. The majority of soils, especially sandy soils, do not need 7 hours." In other words, 7 hours is the maximum required. Well, similarly for my machine, the 3 hours mentioned is a maximum time requirement. The average soil can be successfully treated in a much shorter time. Mr. Fletcher also states that even if 7 hours are used it is no loss of time to the operator, because he is busy anyway. Certainly, in this age of conservation and efficiency engineering, one should not countenance waste of power and energy in running a machine longer than necessary!

Another argument not as yet presented may be stated here. In the Bureau machine the bottles are in a horizontal position. With a moderate jerking back and forwards of the bottle only the upper portion of the soil is shaken; with more vigorous jerking the whole mass of soil is in movement, but, on account of the friction on the bottle, the lower part moves more slowly than the upper, and may move but slightly or not at all. Also, in order to have all the sample in action at the same time the upper portion is driven backwards and forwards with more violence than it really requires. As a result, there is a tendency for the particles to abrade one another. Obviously this breaking down of the soil particles should not be very appreciable or the method is a failure. In treatment by my machine the

bottle is slowly ended over and over. The whole sample thus falls from one end of the bottle to the other through a column of water twice in every revolution of the wheel. The lack of violence in the process of "merely pouring," coupled with shorter time of treatment, reduces abrasion to a negligible factor. It should be clear why my method is shorter than the Bureau method for all the particles are receiving equal treatment all the time.

FREEMAN WARD

SHEFFIELD SCIENTIFIC SCHOOL, YALE UNIVERSITY  
NEW HAVEN, CONN., October 16, 1914

## AMERICAN INSTITUTE OF CHEMICAL ENGINEERS 7TH ANNUAL MEETING, PHILADELPHIA DECEMBER 2-5, 1914

### PROGRAM OF PAPERS

- Address of Welcome. MAYOR BLANKENBURG.  
Distribution of Industrial Opportunities. GEORGE OTIS SMITH, Director of the U. S. Geological Survey.  
The Manufacture and Application of the Artificial Zeolites (Permutite) in Water Softening. D. D. JACKSON.  
Feldspar as a Possible Source of American Potash. ALLERTON S. CUSHMAN AND GEO. W. COGGESHALL.  
Hydrometallurgical Apparatus and Its Use in Chemical Engineering. JOHN V. N. DORR.  
The Hardwood Distillation Industry. E. H. FRENCH AND JAMES R. WITHROW.  
The Chemical Industries of Japan. JOKICHI TAKAMINE.  
Need of Up-to-date Manufacturing Statistics. BERNHARD C. HESSE.  
Ore Flotation, a New Hydrometallurgical Development. S. P. SADTLER AND S. S. SADTLER.  
Aspects of Some Chemical Industries in the United States Today. EDWARD GUDEMAN.

### EXCURSIONS

Atlantic Refining Co. of the Standard Oil Co. at Point Breeze on the Schuylkill River. This plant has the new Burton process for the distillation of petroleum and the manufacture of motor fuel.

United Gas Improvement Co. This plant has new water gas generators with waste heat boilers. The physical research laboratory was visited and recent developments in artificial illumination and photometric apparatus were inspected.

Welsbach Works, Gloucester, N. J. Nitrating and colloid manufacture, thorium nitrate and mantle manufacture, solvent recovery, metal working, nickel plating and finishing were seen.

New York Shipbuilding Co., Camden, N. J.

Farr & Baily Linoleum Works, Camden, N. J.

Commercial Museums, West Philadelphia. Address by Dr. Wm. P. Wilson on the work of the Museum.

Laboratories of the University of Pennsylvania.

Barrett Manufacturing Co., Chemical Department, Frankford, Philadelphia. The working up of the light and middle oils, the refining of naphthalene, the small scale preparation of carboic acid, etc., were shown.

## COMMUNICATION FROM THE ANALYTICAL COMMITTEE RUBBER SECTION, AMERICAN CHEMICAL SOCIETY

From the reply of The Joint Rubber Insulation Committee, THIS JOURNAL, 6, 515, it is evident that some discussion of the results as published in THIS JOURNAL, 6, 514, is necessary to prevent any misunderstanding as to their bearing. Since this reply appeared it was impossible to hold a meeting of The Analytical Committee until this date.

In presenting the results of their work, The Analytical Committee voted to confine their published report to the facts brought out by their analysis and omit all discussions, as a publication of these discussions in full would have occupied more space than this committee could reasonably have asked for and it was by no means certain how much of it would be of general interest.

<sup>1</sup> U. S. Dept. Agr., Bur. Soils, Bull. 84, p. 15.



The three compounds selected for analysis were designed to test the accuracy of the methods for analysis of the Acetone Extract as affected by the presence or absence of the two hydrocarbons used in commercial practice. The amount of rubber and the fillers were varied only slightly to avoid the influence of extraneous factors on the results. The selection of fillers and the respective proportions were designed to fall within the limits prescribed by the 1913 Railway Signal Association's specification for 30% Fine Para insulation, as this was considered to be the most important type of material to which the methods of The Joint Rubber Insulation Committee were likely to be immediately applied. The methods of The Joint Rubber Insulation Committee were intended to be applicable to the analysis of just such compounds. Therefore, if the errors have been magnified due to the constituents, the methods should be revised to meet such conditions.

The Analytical Committee, before issuing its report, took into consideration the discrepancies of Analyst No. 3 under waxy hydrocarbon, which in all probability were due to the Solution of Alcoholic Potash used. They also took into consideration the results of No. 4, under Free Sulfur, which were obtained by the use of a different type of extractor, for comparative purposes. Inasmuch as no conclusions drawn from either of these results were adverse to the methods of The Joint Rubber Insulation Committee, no exception was made to the decision of the committee to publish only the results and conclusions.

These discrepancies and the reasons for the same were brought to the attention of the Rubber Section at the Cincinnati meeting and were fully discussed at that time. Two members of The Joint Rubber Insulation Committee, who were instrumental in drawing up the comments printed in THIS JOURNAL, 6, 515, were present at this meeting and were fully acquainted with the facts.

A clerical error which appeared in the published report should be corrected as follows: Under Sample A, Analyst I:

11/20—Total waxy hydrocarbons should read 2.14 per cent

11/21—Total waxy hydrocarbons should read 2.55 per cent

Referring to the comments on the work of Analyst No. 2,

The Joint Rubber Insulation Committee state, "The results indicate that the Acetone Extraction was not properly made." Comparison of the results of Analyst No. 2 with those of Nos. 1, 4 and 5, which are taken as a standard for comparison, does not substantiate this statement, as these results are consistent with Nos. 1, 4 and 5 and the duplicate results are particularly consistent; furthermore, the analyst states that the Acetone Extraction was made absolutely in accordance with the procedure.

The fact that the averages of a large number of determinations are "about what we would expect from this compound" proves only that positive and negative errors are equally probable and does not substantiate the claim that the determination of saponifiable extracts by this method will give accurate results, since the individual results show that the probable error of a single determination is large.

This procedure is given as a method for 30 per cent Hevea rubbers, therefore the Analytical Committee was justified in making its first investigation on Fine Para.

E. W. BOUGHTON G. H. SAVAGE P. H. WALKER  
W. A. DUCCA J. B. TUTTLE D. W. WHIPPLE, *Chairman*

114 LIBERTY ST., NEW YORK CITY  
November 16, 1914

### THE SPECIFIC HEAT OF CALIFORNIA PETROLEUMS A CORRECTION

In my article under the above title in THIS JOURNAL, 6, 727, the formula used for the calculation of the specific heats given in the results was  $c = \frac{CM(T - t) - W}{m(t - t_0) - m}$  and not that given in the article as originally printed.

3333 19TH STREET  
SAN FRANCISCO, CAL., November 7, 1914

HAROLD E. WALES

### THE EXPLOSIBILITY OF GRAIN DUSTS—A CORRECTION

In the article printed under the above title, in THIS JOURNAL, 6, 934, the name of Mr. David J. Price as joint author was omitted by error.

HAROLD H. BROWN

BUREAU OF CHEMISTRY, WASHINGTON  
November 16, 1914

## PERSONAL NOTES

The University of Pittsburgh announces the following course of Special Evening Lectures on Chemical Engineering during 1914-15: Nov. 9th—"Our New Knowledge of Coal," H. C. Porter, Chemist, U. S. Bureau of Mines, Pittsburgh. Nov. 16th—"Recent Researches on the Combustion of Coal," Henry Kreisinger, Engineer in Charge of Fuel Tests, Bureau of Mines, Pittsburgh. Nov. 23rd—"Some Applications of Pulverized Coal," Richard K. Meade, Consulting Chemist, Baltimore. Nov. 30th—"Producer Gas," J. K. Clement, Physicist, Bureau of Mines, Pittsburgh. Dec. 7th—"The Softening of Water for Industrial Purposes," James O. Handy, Director of Research, Pittsburgh Testing Laboratories. Dec. 14th—"The Classification of Clays," Edward Orton, Head of Department of Ceramics and Dean of the College of Engineering, Ohio State University. Jan. 4th—"The Effect of Heat on Clays," A. V. Bleining, Director Technological Laboratory, U. S. Bureau of Standards, Pittsburgh. Jan. 11th—"The Manufacture of Structural Clay Products," A. V. Bleining. Jan. 18th—"The Manufacture of Refractories," Kenneth Seaver, Chief Chemist, Harbison-Walker Refractories Co., Pittsburgh. Jan. 25th—"The Manufacture of Porcelain," Ross C. Purdy, Chief Chemist, Norton Co., Worcester, Mass. Jan. 25th—"Glazes and Enamels," A. V. Bleining. Feb. 1st—Symposium: "Special Phases of the Glass Industry," C. H. Kerr, Pittsburgh Plate Glass Co.; S. R. Scholes,

Assistant Director Mellon Institute of Industrial Research; Alexander Silverman, University of Pittsburgh. Feb. 8th—"Special Methods of Pyrometry," H. S. Stupakoff, Director Stupakoff Laboratories, Pittsburgh. Feb. 15th—"The Present Status of the Chemical Technology of Vanadium," B. D. Saklat-Walla, Chief Chemist, American Vanadium Co., Pittsburgh. Feb. 22nd—"The Manufacture of Steel Tubing," F. N. Speller, National Tube Co. Mar. 1st—"The Manufacture of Steel in the Electric Furnace," F. Crabtree, Professor of Metallurgy, Carnegie Institute of Technology. Mar. 8th—"The Corrosion of Iron and Steel," D. M. Buck, American Sheet and Tin Plate Co., Pittsburgh. Mar. 15th—"Catalysis," M. A. Rosanoff, Professor of Research Chemistry, Mellon Institute. Mar. 22nd—"Recent Developments in the Electrochemistry of Organic Compounds," Harold Hibbert, Research Fellow, Mellon Institute; and "Industrial Applications of the Phase Rule," M. A. Rosanoff.

The North Carolina College of Agriculture and Mechanic Arts has made the following additions to the staff of its Chemistry Department: C. F. Miller, E. L. Frederick, J. T. Dobbins and H. L. Cox.

Mr. James J. Bajda, formerly connected with the Chemical Department of Sulzberger & Sons, is now Chemist and Chemical Engineer for the San-I-Genic Company of Winnipeg, Canada.

J. D. Mackenzie is now employed in the laboratory of Armour and Company at Chicago.

Mr. W. D. Richardson, of Swift & Co., Chicago, spent his vacation bear hunting in Oregon.

Prof. M. A. Rosanoff, for the past seven years director of the Department of Chemistry in Clark University, has accepted a professorship of Chemical Research in the Mellon Institute of Industrial Research and the Graduate School of the University of Pittsburgh.

Dr. Harvey W. Wiley celebrated his seventieth birthday recently by a dinner party. Among the guests were Prof. Chas. E. Munroe, one of Dr. Wiley's instructors at Harvard; Dr. W. D. Bigelow, for many years with Dr. Wiley in the Bureau of Chemistry; Dr. G. L. Spencer, a student under Dr. Wiley at Purdue University 40 years ago, and Prof. Frank W. Clarke, of Washington.

The Royal Canadian Institute in Toronto, Canada, plans to inaugurate work on the lines of the Mellon Institute of the University of Pittsburgh. Dr. Raymond F. Bacon, director of Mellon Institute, was invited to address the Canadian Institute and spoke before them on "Industrial Research" on November 7th. The lecture was given in the University of Toronto, the alma mater of the late Dr. Robert Kennedy Duncan, founder of the system of industrial research at the Mellon Institute.

Prof. J. H. Mathews, of the University of Wisconsin, will give an illustrated lecture on "Color Photography" before the Kansas City Section of the A. C. S. on December 12th.

The program for the December 11th meeting of the New York Section of the A. C. S. is as follows: "A Surficial Burn, Produced by an Unknown Radiation," C. A. Doremus; "Past, Present and Future of Electrochemistry in America," E. F. Roeder; "Research in Applied Chemistry," W. H. Walker; "Industrial Research," Raymond F. Bacon.

The Executive Committee of the International Congress of Mining, Metallurgy, etc., London, 1915, decided on September 4th to adjourn the holding of the Congress *sine die* on account of the war.

Prof. J. G. Shearer gave an illustrated lecture on "Some Phases of the Development of Roentgen Rays and Their Applications," before the Cornell Section of the A. C. S., on November 16th.

Mr. Carl Hambuechen, of the American Carbon and Battery Co., addressed the November 9th meeting of the St. Louis Section of the A. C. S. on "Some Problems in the Manufacture of Dry Batteries."

The Hedley F. Jobbins glycerine plant at Aurora, Ill., and one of the largest of its kind in the world, was completely destroyed by fire on August 23rd. The loss of a very well equipped laboratory and the destruction of hundreds of tons of finished glycerine made the fire an exceedingly costly one.

The New York Section of the American Electrochemical Society met in joint session with the American Gas Institute and the Illuminating Engineering Society on November 18th. The topic for the evening was "The Effect of Chemical Research on Lighting," and the speakers were: H. S. Miner, W. C. Moore, R. E. Myers, R. D. Bailey, D. MacFarlan Moore and H. E. Ives.

Dr. P. F. Trowbridge, of the University of Missouri, spoke on "Some Problems in Nutrition," on November 9th, at the University of Rochester, before the Rochester Academy of Science and the Rochester Section of the A. C. S.

At the October 31st meeting of the Puget Sound Section of the A. C. S. at Seattle, the following articles were read: "Fish Oils," J. W. Brandt; "Fertilizer and Other By-Products of the Fishing Industry," E. A. Stoppel.

The Maryland Section of the A. C. S. held its 2nd regular meeting on November 14th. Papers were read by J. Bosley Thomas, "Present and Future Methods for the Purification of the Baltimore City Water Supply," and Wm. Royal Stokes, "Bacteriological and Sanitary Results Obtained by the Treatment of the Baltimore City Water Supply."

The following papers were read at the Connecticut Valley Section of the A. C. S. in Hartford on November 7th: "Recent Studies on the Theory of Dyeing and the Chemistry of Wool Fiber," Frederic Dannerth; "The Control of Plating Solutions," Arthur DeF. Cowpertwait.

Prof. Harry McCormack, of Armour Institute of Technology, lectured on November 13th before the Chicago Section of the A. C. S. on "Why We Do Not Manufacture Aniline Dyes."

The Eastern N. Y. Section of the A. C. S. met at Union College, Schenectady on October 30th. The following papers were presented: "The Commercial Production of Oxygen and Nitrogen," G. L. Fonda; "The Influence of Composition on the Magnetic Properties of Steel," W. E. Ruder.

The Highway Engineering Department of Columbia University offers the following illustrated lectures during December, 1914: Dec. 3rd—"Specifications for Sizes and Physical Properties of Broken Stone," Arthur W. Dean, Chief Engineer, Mass. Highway Commission. Dec. 7th—"The Essential Physical and Chemical Properties of Creosote Oils for Wood Blocks," S. R. Church, Manager Research Department, Barrett Manufacturing Co., New York. Dec. 9th—"Details of Construction of American Wood Block Pavements," A. W. Dow, Chemical and Consulting Paving Engineer, New York. Dec. 11th—"European Wood Block Pavements," George W. Tillson, Consulting Engineer to the President of the Borough of Brooklyn, New York. Dec. 14th—"The Construction and Maintenance of Cement-Concrete Pavements," Edward D. Boyer, Cement and Concrete Expert, The Atlas Portland Cement Co., New York. Dec. 16th—"Specifications for Physical Properties of Paving Bricks and Stone Blocks," William A. Howell, Engineer of Streets and Highways, Newark, N. J. Dec. 23rd—"Planning of Streets and Street Systems," Nelson P. Lewis, Chief Engineer, Board of Estimate and Apportionment, New York. Dec. 28th—"Production of Bermudez and Trinidad Asphalts," C. N. Forrest, Chief Chemist, Barber Asphalt Paving Co., Maurer, N. J. The program of the November 16th meeting of the Rochester Section of the A. C. S. was as follows: "Notes on the Determination of Antimony," H. E. Howe; "Some of the Impurities of Photographic Chemicals," M. B. Punnett; "Military Explosives," C. E. K. Mees.

Dr. Edgar Fahs Smith, Provost of the University of Pennsylvania, addressed the Philadelphia Section of the A. C. S. at its November 19th meeting.

Mr. F. B. Sherwood, B.S. 1912, North Carolina A. & M. College, has been appointed Assistant Chemist to the North Carolina Agricultural Experiment Station.

The program of the Wisconsin Section of the A. C. S. for November 18th included the following papers: "Apparatus for Precise Cryoscopic Measurement at Elevated Temperatures," Prof. J. H. Mathews; "The Effect of Temperature Control in the Destructive Distillation of Wood," R. C. Palmer.

Dr. Alfred Springer gave an illustrated lecture on "An Egyptian Trip," before the Cincinnati Section of the A. C. S. on October 28th.

A series of seven lectures on "Sanitation as Applied to Cities" was given during November at the Worcester Polytechnic Institute, by Prof. George C. Whipple, of Harvard University.

Mr. Chas. Boulton, of the Carborundum Co., gave an illustrated lecture on carborundum before the Columbus Section of the A. C. S. on November 5th.

Prof. Harry McCormack is giving a course of lectures on "Industrial Chemistry" at Armour Institute of Technology; these lectures are given on Tuesday evenings, from 7.30 to 9.30 o'clock, and the course will continue for three terms.

Dr. George Oliver Curme, of Evanston, Ill., was one of few Americans abroad this summer who successfully escaped the war embargo. He arrived in this country at about the time the storm broke in Belgium. Dr. Curme was in Berlin doing some special work in chemistry. He took his doctor's degree at Chicago in 1913 and went abroad shortly afterwards.

Mr. H. E. Jordan gave an illustrated lecture on "Some Features of Water Purification before the Indiana Section of the A. C. S. on November 14th.

The Milwaukee Section of the A. C. S. met on November 20th. Prof. E. B. Hart, of the College of Agriculture, University of Wisconsin, spoke on "Recent Developments in Agricultural Chemistry."

At the November 11th meeting of the Lexington Section of the A. C. S. the following papers were given: "Some Curiosities of Chemical Literature," Dr. Garnett Ryland; "Note on a Specimen of Vivianite from Marshall Co., Ky.," Dr. A. M. Peter.

Dr. Charles H. Viol, Director of the Radium Research Laboratory, Pittsburgh, gave an illustrated lecture on Radium and Radioactivity before the Pittsburgh Section of the A. C. S. on November 12th.

The N. Y. Section of the Society of Chemical Industry were addressed by John H. Hall on "Manganese Steel" and by George F. Comstock on "Titanium and Its Effects on Steel" at their meeting on November 20th.

Mr. W. R. Gilard has resigned as Chemist with the Pittsburgh Testing Laboratory to accept a position as research chemist with the Pittsburgh Plate Glass Co.

On invitation of the Brown Chapter of the Society of the Sigma Xi, the Rhode Island Section of the A. C. S. attended an illustrated lecture on "X-Rays and Crystals" on November 20th by William Henry Bragg, A.M., F.R.S., Professor of Physics in the University of Leeds, England.

The U. S. Bureau of Mines has begun the collection of a general library of petroleum literature, under the direction of W. A. Williams, chief petroleum technologist. The details of this work have been assigned to Dr. David T. Day, recently transferred from the U. S. Geological Survey as petroleum technologist, who will also assist in a thoroughly organized research into the chemistry of oils, which is being developed by the Bureau of Mines. In view of the importance of such a library, the Bureau hopes that all technologists will aid in the work by exchanging with it all available books and maps on the subject.

Dr. Frederick B. Power will retire from the directorship of the Wellcome Chemical Research Laboratories, London, on December 1st, in order to return to the United States, where, for family reasons, he will make his future home.

Dr. Frank L. Pyman, whose researches and contributions to chemical science are well known, will succeed Dr. Frederick B. Power as director of the Wellcome Research Laboratories, London, England.

President A. C. Humphreys, of the Stevens Institute of Technology, will act as president of the International Gas Congress, which meets in San Francisco next September.

## GOVERNMENT PUBLICATIONS

By R. S. McBRIDE, Bureau of Standards, Washington

**NOTICE**—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate. Consular Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington. The regular subscription rate for these Consular Reports mailed daily is \$2.50 per year, payable in advance, to the Superintendent of Documents.

### GEOLOGICAL SURVEY

**Production of Anthracite in 1913.** EDWARD W. PARKER. Advance chapter from Part 2, Mineral Resources, 1913. 16 pp. Including the coal recovered from old culm banks by washeries, and a small quantity dredged from Susquehanna River, the production of anthracite in 1913 amounted to over 81 million long tons valued at \$195,000,000. This is an increase of nearly 10 per cent over the production of the previous year. No unusual influence affected the 1913 trade but the increase is rather greater than average. "The increase in the use of artificial gas and of coke for domestic purposes will probably keep pace with the increase of population in the markets supplied by anthracite, and there is little probability that the production of anthracite will show any marked increase in the future. Changes in temperature and labor conditions will continue to be the most important factors affecting the production of anthracite." The standard screens used in the preparation of anthracite have the following dimensions, the percentage of the total production of each size being indicated in the last column:

### STANDARD SIZES OF ANTHRACITE

Size	Through	Over	Percentage of total production
Lump and steamboat.....			0.51
Broken or grate.....	4 inches square	2½ inches square	4.92
Egg.....	2½ inches square	2 inches square	12.59
Stove.....	2 inches square	1½ inches square	19.53
Chestnut.....	1½ inches square	1 inch square	24.08
Pea.....	1 inch square	¾ inch square	11.51
Buckwheat No. 1.....	¾ inch square	½ inch square	13.33
Buckwheat No. 2 or rice.....	½ inch square	¼ inch square	7.90
Buckwheat No. 3 or barley.....	¼ inch square	⅛ inch round	5.17
Screenings.....	⅛ inch round		0.46

**Production of Peat in 1913.** CHARLES A. DAVIS. Separate from Part 2, Mineral Resources, 1913. 19 pp. "Up to the present time, however, practically none of these attempts (in the U. S.) at the production of a serviceable fuel from peat have been commercially successful." However, in almost every case, where material properly prepared has been offered for sale, it has found a ready market at prices which were ample to have paid a profit upon the operation. European methods for the production of peat in form suitable for fuel either as "cut peat" or "machine peat" are described. The various processes for pressing water from peat and briquetting it are also described. Despite the general belief to the contrary it should be noted that "only a single peat-briquette factory is known to be in operation in Europe at the present time." Among the various uses for peat discussed are the following: Peat powder, peat coke or charcoal, as fuel for steaming, as fuel for producer-gas generation, as fuel in special industries, as fertilizer filler or as fertilizer (the latter in case of peats rich in combined nitrogen), stock food, paper stock, and stable litter. The production in 1913 in short tons for the various purposes shows as follows: Fertilizer 28,400,000, valued at



\$169,600; for stock food 4,800,000, value \$27,600; and for stable litter, all of that being imported material, 10,983, valued at \$55,719.

**Barytes.** JAMES M. HILL. Separate from Part 2, Mineral Resources, 1913. 10 pp. The production of crude barytes in the United States in 1913 was 45,298 short tons valued at \$156,275, an increase of 20 per cent in quantity over 1912. The average price per ton in 1911 was \$3.19, in 1912 \$4.09, and in 1913 \$3.45. However, it is noted that considerable difference in average price per ton is found for the production in different localities, that in Missouri reaching \$3.78 per ton in 1913, whereas that of Tennessee and Kentucky was only \$1.70 per ton for the same period.

The 1913 imports of unmanufactured barytes amounted to \$61,000; the manufactured product amounted to \$38,000. The imports of barium compounds during the same period were as follows:

Barium carbonate, natural.....	\$ 13,116
Barium carbonate, manufactured.....	38,949
Barium binoxide.....	239,000
Barium chloride.....	37,620
Blanc-fixe, or artificial barium sulfate.....	62,785
Total.....	\$391,470

This report describes the mineral characteristics, the uses and the occurrence of barytes in the United States.

**Strontium.** JAMES M. HILL. Note from Mineral Resources, 1913. During 1913 no strontium was reported as mined in the United States, probably because of the limited market. "No strontium carbonate, oxide, or protoxide was imported in either 1911 or 1912, but in 1913 the total value of imports of these salts was \$2,284. Probably some strontium nitrate was imported for use in 'red fire,' but it is not possible to obtain figures of the imports of any salts of strontium except those named above."

**The Production of Salt, Bromine, and Calcium Chloride in 1913.** W. C. PHALEN. 16 pp. The marketed production of salt in 1913 was over 34,000,000 barrels of 280 pounds each, having a total value in excess of \$10,000,000. It is noted that the price of salt has been slowly rising throughout the last several years. A classification is given of the several methods of production, and the production by grades and by localities is given in detail. It is noted that a total value of imported salt was \$421,745 and the exports \$515,194 during 1913.

The production of bromine in 1913 amounted to 572,400 pounds having a value of about \$110,000. The calcium chloride production in the same period was 19,611 short tons valued at \$130,000.

**Asbestos.** J. S. DYLLER. Separate from Part 2, Mineral Resources, 1913. 16 pp. "The production of asbestos in the United States is small, but in manufactured asbestos products the United States surpasses any other country. The total output of asbestos in this country for 1913 was about 1,100 short tons, and all of it came from 2 producers in Georgia and 1 in Arizona." Not only was the production very much less during this period but the value per ton (\$10) was also lower than in any previous year, except 1907. As a matter of fact, the price of asbestos in the United States is controlled by the Canadian market, since the world's supply of asbestos is largely drawn from the province of Quebec; however, a rapid development of the Russian asbestos is making that country an important factor. It is noted that an advance of 10 per cent to 15 per cent in price is to be expected during 1914, owing to the demands for increase in wages. The asbestos imported in 1913 amounted to \$2,307,666, nearly 90 per cent of this being unmanufactured material. The occurrence and character of asbestos found in this country, as well as the Canadian and Russian deposits, are given in some detail and the summary of some recent investigations concerning these asbestos is included.

**The Gypsum Industry in 1913.** RALPH W. STONE. Separate from Part 2, Mineral Resources. 17 pp. In 1913 over 2,500,000 short tons of raw gypsum were mined, this being an increase of about 4 per cent over the previous year. The applications of this product are shown by the following table, which indicates the application of the marketed product of gypsum in the United States during 1913:

SOLD CRUDE	Quantity	Value	Average price per ton
For Portland cement.....	408,221	\$ 600,913	\$1.47
As land plaster.....	54,815	95,953	1.75
For other purposes.....	100	200	2.00
Total.....	463,136	\$697,066	\$1.51
SOLD CALCINED			
As plaster of Paris, wall plaster, Keene's cement, etc.....	1,680,137	5,858,785	3.49
For dental plaster.....	861	4,168	4.84
To glass factories.....	10,942	21,797	1.99
For Portland cement and other purposes.....	81,889	193,006	2.36
Total.....	1,773,849	\$6,077,756	\$3.43

The report also includes a discussion of the production of other countries, trade and manufacturing conditions, the character of gypsum products made, and the occurrence of gypsum and gypsite in the United States.

**The Production of Fluorspar and Cryolite.** ERNEST F. BUCHARD. Separate from Part 2, Mineral Resources, 1913. 8 pp. The total quantity of domestic fluorspar reported as marketed in 1913 was 115,580 short tons, valued at \$736,000. This was a slight decrease as compared with the previous year. The conditions of the industry, the character and composition of the supply which has been marketed, the uses of fluorspar, and the occurrence are described in some detail.

As a note, the imports and prices of cryolite are given as follows:

"No cryolite is produced in the United States, the entire supply used in this country being imported from Ivigtut, an Eskimo hamlet on the southern coast of Greenland.

"The quantity of cryolite reported to have been imported for consumption into the United States in 1913 was 2,559 long tons, valued at \$52,557, as compared with 2,126 long tons, valued at \$48,293, in 1912. The average price per ton declared in 1913 was apparently \$20.34, as compared with \$22.72 in 1912. Cryolite was imported free of duty in 1913."

**The Production of Mineral Waters in 1913 with a Discussion of their Radioactivity.** R. B. DOLE. 48 pp. The statistics given in this report are intended to include natural waters that are bottled and sold in practically their natural state, but it is not intended to include natural still waters that have been changed materially in chemical character or waters that are sold by flat or meter rates. No distinction has been drawn between the "table water" and "medicinal water," since the practice in differentiating by these two varies greatly. There are 746 commercial springs reporting, which indicate over 62,000,000 gal. sold at an average price of 11 cents per gal. About one-third the total value is classed commercially as "medicinal water." The range in price indicated shows a few springs selling at less than 2 cents or over 50 cents per gal.; the large majority, however, are between 2 cents and 10 cents. The imports in 1913 amounted to 3,364,000 gal., valued at \$950,000. The report gives in great detail the production by states indicating the name and location for all springs reporting.

In the portion discussing the radioactivity of mineral waters, the methods of measurement of radioactivity and the units used are briefly discussed, and a tabulation is given indicating the radioactivity of the considerable number of spring waters in this country and in Europe. A brief bibliography is appended.

**The Production of Magnesite in 1913.** CHARLES G. YALE AND HOYT S. GALE. Separate from Part 2, Mineral Resources, 1913. 14 pp. The 1913 production of magnesite was over 8

per cent less than in 1912, being 9,600 short tons valued at \$77,000. The report indicates the sources, prices, imports, and traffic regulations regarding this mineral. The more important uses of magnesite are indicated as follows: Refractories; in paper-making as bisulfite; for the manufacture of carbon dioxide; as oxychloride or "Sorel" cement. These and miscellaneous applications are discussed, particular attention being given to magnesite cement which is discussed in detail.

**Statistics of the Pottery Industry, 1913.** JEFFERSON MIDDLETON. Separate from Part 2, Mineral Resources, 1913. 15 pp. In this report are given full data as to the production of various classes of pottery in different parts of the United States. The value of all domestic pottery marketed in 1913 was approximately \$38,000,000, an increase of more than 4 per cent over 1912. The imports, which combine almost exclusively high-grade work, show a slight increase over the previous year, amounting to about \$10,000,000.

**Clay Products of the United States.** JEFFERSON MIDDLETON. Special tabulation without number. 1 p. This circular gives the value, quantity, and average price per unit for various kinds of brick, tile, terra cotta, and other clay products produced during 1913. The total value is in excess of \$181,000,000. Data are given separately for each of the several states.

**Production of Spelter in 1913.** C. E. SIEBENTHAL. Special leaflet, unnumbered. This circular indicates the variation in price of spelter at London and at St. Louis. Of 60 per cent of zinc concentrates at Joplin there is shown the weekly sales for the period 1906-1913, inclusive. The zinc smelting capacity of each of the various plants reporting is indicated, and tables are given showing the production by states and by foreign countries for the same period. In 1913 the primary spelter produced amounted to 346 tons; the consumption of primary spelter in the United States was less than 300,000 tons; the world's production of spelter was 1,100,000 tons.

**Quicksilver Production in 1913.** H. D. McCASKEY. 15 pp. The production indicated for 1913 amounts to 20,213 flasks of 75 pounds each, valued at \$813,000, the large majority of the product coming from California. Owing to the low prices during the year, the quicksilver industry was even less prosperous in 1913 than in the previous year. It is of particular interest to note that "the market has been very quiet during the last two years and some large producers are understood to have stored some of their output from time to time and others to have reduced their production until the demand and prices for the metal improve." Labor legislation for protection of labor in the mines is said to have added somewhat to the difficulty of profitable production in California. Data are given as to the production and resources for the different parts of this country as well as the world's production and the imports and exports. The New York price for 1913 averaged \$39.54 per flask of 75 pounds, about \$3 less than during the previous year.

**Gold, Silver, Copper, Lead, Etc., in 1913.** VARIOUS AUTHORS. Separate from Part 1, Mineral Resources, 1913. Sixteen sections of this volume are devoted to various phases of this subject, some of these being already in print. There are general reports for gold, silver, copper, lead, and zinc and special reports (called Mines Reports) for the several districts of the country arranged as follows: Eastern States, Central States, Alaska, Arizona, California and Oregon, Colorado, Idaho and Washington, Montana, New Mexico and Texas, South Dakota and Wyoming, and Utah. These reports are too detailed to permit of a review. Any of them can be secured as separates as soon as issued.

#### BUREAU OF STANDARDS

**Measurement of Standard of Radiation in Absolute Value.** W. W. COBLENTZ. Scientific Paper 227. 14 pp. Measurements are given of the radiation from the Hefner lamp and from a standard sperm candle relative to that from a black body and

data are given for more refined measurement of radiation from standard incandescent lamps.

**An Experimental Study of the Koepsel Permeameter.** CHARLES W. BURROWS. Scientific Paper 228. 30 pp. Of interest in the study of that type of instrument for use in accurate measurements of permeability and hysteresis curves.

**Various Modifications of Bismuth-Silver Thermopiles Having a Continuous Absorbing Surface.** W. W. COBLENTZ. Scientific Paper 229. 57 pp. This paper is largely of physical interest, but the construction of thermopiles is fully discussed, and appendices are included which take up the following subjects: Galvanometer mirrors, vacuum galvanometers, the most efficient combination of thermopile and galvanometer resistance, test of stellar thermoelements on stars, the maintenance of high vacua by means of metallic calcium.

**Lead Acetate Test for Hydrogen Sulfide in Gas.** R. S. McBRIDE AND J. D. EDWARDS. Technologic Paper 41. 46 pp. The effect of practically all the factors which can influence the sensitiveness of the test when utilized in a commercial way for the testing of a city gas supply has been examined. The method of testing recommended is intended for commercial use and not for the most precise scientific work. However, the experiments described in detail indicate the methods of varying the test to make it of greatest sensitivity.

**Testing of Electrotpe Solutions.** Preliminary circular, unnumbered. 4 pp. This circular indicates in a preliminary way the general problems met in the control of copper electrotyping solutions and gives in simple form preliminary suggestions for maintenance of the proper acidity and density of the solutions. No new experimental work is reported since the circular is intended to aid only non-technical operators in commercial plants.

#### BUREAU OF MINES

**Production of Explosives in the United States during 1913.** ALBERT H. FAY. Technical Paper 85. 15 pp. For purposes of comparison, explosives are grouped as black blasting powder, high explosives and permissible explosives. The production is given by states for these 3 groups. The totals reported are as follows: Black blasting powder, 194,146,000 lbs.; high explosives, other than permissible, 241,682,000 lbs.; and permissible explosives, 27,685,000 lbs.; a grand total of 463,514,000 lbs. The coal production per pound of explosives in 1913 was 2.72 tons, an increase of 0.36 ton over 1913.

**A Study of the Oxidation of Coal.** HORACE C. PORTER AND O. C. RALSTON. Technical Paper 65. 30 pp. This paper discusses the oxidation of coal at ordinary temperature, spontaneous heating of coal, the initial action of oxygen on coal, factors affecting the ignition of coal and affecting the rate of oxidation of coal, and closely related topics; analyses are given of the coals tested to indicate the nature of the change.

#### CONSULAR REPORTS—OCTOBER, 1914

The war has offered a market for American oleomargarine in England. Oleomargarine used in Europe usually consists of a mixture of cottonseed and copra (cocoanut) oil. (P. 13.)

As practically all the copra (dried cocoanut) from the Philippines was formerly shipped to France, the price has fallen to practically nothing, so that efforts are being made to develop a market in the United States. (P. 14.) See also P. 411 for a description of the copra industry of the Philippines.

Uranium ores are being prospected in India. (Pp. 20, 335.)

The output of the Government iron foundry at Walamatsu, Japan, amounts to 216,000 tons, and will soon be increased to include galvanized iron. (P. 24.)

The manufacture of buttons from ivory nuts, formerly carried out in Germany, should be a profitable industry in the United States. (P. 104.)

The methods of **graphite** mining in Ceylon are described. (P. 164.)

A committee appointed by the British Government has recommended among others the following regulations for **patent medicines**, viz., (1) control by one department under the ministry of Public Health, (2) registration of the composition of all patent medicines, to be confirmed by confidential government analyses, (3) prohibition of the sale of any objectionable patent medicines; (4) that pure drugs sold under patent names be no longer exempt from duty. (P. 278.)

The **camphor industry** of India is described. (P. 288.)

Efforts are being made to develop the **petroleum** resources of India. (P. 443.)

The principal imports of **graphite** into the United States come from Ceylon, Mexico, Canada and Japan. (P. 455.)

**Tungsten ore** is being mined in Siam, the output in 1912-13 being over 300 tons. (P. 460.)

The **manganese ore** industry of Brazil is described. (P. 476.)

**Carnauba wax**, obtained from the leaves of the carnauba palm, is one of the principal exports of Brazil to the United States. It is used for the manufacture of phonograph records, shoe polish, candles, etc. (P. 477.)

Newly organized industries in Trinidad, include a **cassava starch factory**, a **cocoanut fiber factory**, and a **tannery**. (P. 489.)

#### RECENT DEMANDS FOR AMERICAN GOODS (PP.)

NOVA SCOTIA—70	NEW BRUNSWICK—219	AZORES—311
Glass	Window glass	Caustic soda
Drugs	Sheet zinc	Cement
Chemicals	Pig lead	Cornstarch
Earthenware	Block tin	Electrical supplies
Yak	White lead	Fertilizers
Vegetable parchment	Zinc white	Glassware
PANAMA—80 and 155	Galvanized iron	Hardware
Sugar	Sulfur	Ink
Glassware	Linseed oil	Linoleum
China	Tin plate	Lubricating oil
Aluminum ware	Cream of tartar	Paints
ONTARIO—108, 138	SPAIN—224	Soap
Carbolic acid	Carbolic acid	Sugar
Oxalic acid	Formic acid	Tallow
Citric acid	Naphthalene	Varnishes
Salicylic acid	Alum	NORWAY—315
Tartaric acid	Aniline dyes	Chemicals
Camphor	Dextrin	Copra
Cocaine	Glass	Dyestuffs
Codine	Copper and iron ware	Rubber
Cream of tartar	Oxide	Iron and steel products
Glycerine	Soda	Sugar
Hydroquinone	Thermometers	Linoleum
Menthol	Waxes	Linseed oil
Morphine	China clay	Olive oil
Castor oil	Emery	Salt
Potassium chlorate	SWEDEN—246	Soda
Potassium permanganate	Coal	Sulfur
Shellac	NEW ZEALAND—259	Tin plate
Sodium benzoate	Drugs	PARAGUAY—372
Sodium salicylate	Chemicals	Drugs
Santonine	Glassware	Electrical supplies
Cottonseed oil	Porcelain	Glassware
PORTUGUESE AFRICA—125	SANTO DOMINGO—273-7	Paper
Cement	Beer	Tinware
Sugar	China	SWITZERLAND—410
Steel	Porcelain	Coal
CHINA—125	Glassware	Coke
Photographic supplies	Iron ware	Petroleum
Paper	Tin	Leather
Drugs	Paper	Iron
Tin	CARTAGENA—347	Steel
Galvanized iron	Drugs	Copper
SWITZERLAND—125	Hardware	Edible oils
Petroleum	Beer	Turpentine
Gasoline	Wines	WEST AFRICA—412
Copper	SWITZERLAND—362	Cement
Tin	Dyestuffs	Hardware
Steel	Petroleum	Glassware
Leather	Gasoline	Earthenware
Coal briquets	JAMAICA—365	Candles
Lead	Condensed milk	Kerosene
Lard	Butter substitutes	COSTA RICA—522
AZORES—140	Beer	Beer
Lubricating oils	Matches	Cement
Soap	Hardware	Condensed milk
Candles	Paints	Sugar
Gelatine	Crockery	Varnishes
Rubber goods	Glassware	Structural iron
	Paper	JAPAN—504
		Hides
		Paper pulp

The **jute industry** of India is prosperous, the United States being the principal consumer. (P. 508.)

The new **oil-bearing nut** discovered in the Philippines has been identified as belonging to the family Meliaceae. The seeds contain 45 per cent of a dark fatty oil. (P. 536.)

The New Zealand Government is attempting to grade **kauri gum**, one of their principal exports to the United States, where it is used in the manufacture of **varnishes**. (P. 540.)

Seeds of the plant "*Jatropha curcas*," cultivated in Argentina, contain 49 per cent of oil, suitable for the **manufacture of soap**. (P. 541.)

The cultivation of the **soya bean** in Argentina is being urged, experiments having shown that it grows well there. (P. 541.)

The **whale oil** industry of Vancouver has had a very successful season. (P. 507.)

The British Government has just purchased 900,000 tons of **raw sugar** in the East Indies at \$97.00 per ton, the largest purchase of sugar ever made. (P. 512.)

**Correction** (see THIS JOURNAL, 6, 965).—The statistics of the U. S. production of dyestuffs which appeared in Daily Consular and Trade Reports for Sept. 16, 1914, included the entire output of dyestuffs and extracts. The production of artificial dyestuffs alone totaled \$1,764,451 in 1904 and \$3,462,436 in 1909.

#### STATISTICS, ETC., ON EXPORTS DURING 1912 AND 1913 TO THE U. S. (PP.)

CETTE, FRANCE—38	VANCOUVER—176	BRITISH SO. AFRICA—232-241 and 357
Argols	Brewer's rice	Hides
Bauxite	Fertilizer	Horn
Glycerine	Glycerine	Chrome ore
Gentian	Gold bullion	Aloes
Rags	Hides	Argols
Verdigris	Whale oil	Berry wax
COAL	Coal	Buchu
Copper ore	Copper ore	Diamonds
VENEZUELA—59	FRENCH OCEANICA—193	ZANZIBAR—261
Balata	Copra	Ebony
Rubber	Phosphate	Ivory
Hides	Vanilla	Skins
Gold	VENEZUELA—193-201	BRITISH HONDURAS—313
Tonka beans	Balsam	Chicle gum
Copaba balsam	Mangrove bark	Hides
Chicle	Bones	Logwood
HULL, ENGLAND—69	Chicle	Rubber
Alum	Copper ore	JAMAICA—368
Ammonium sulfate	Fustic	Annatto
Carbolic acid	Gold	Fustic
Cement	Hides	Hides
Chalk	Rubber	Kola nuts
Cresote	Tonka beans	Logwood
Cresol	St. PIERRE—214	Orange oil
Fertilizers	Fertilizers	JAVA—369
Glue	Fish glue	Benzine
Iron oxide	Skins	Copra
Castor oil	Copra	Cubeb
Cresote oil	SAMOA—218	Damar
Linseed oil	Copra	Gambier
Rape oil	BERMUDA—252	Peanuts
Soya bean oil	Arrow root	Gum benzoin
Sunflower oil	Hides	Gum copal
Paints	TRIPOLI—298	Gutta percha
Ultramarine	Hides	Hides
Whiting	NUREMBERG, GER-	Kapok
PERNAMBUCO—84	MANY—310	Citronella oil
Castor beans	Cigar lighters	Quinine
Hides	Bronze	Rubber
Rubber	Electric carbons	Sugar
Carnauba wax	Lupulin	Tapioca
ARGENTINE—88	Drugs	Vanilla
Linseed	Percussion caps	Paraffin wax
Hides	Optical glass	TRINIDAD—404
Inebacho logs	Mirror glass	Asphalt
Inebacho extract	Plate glass	Bitters
SAN SALVADOR—132	Gold leaf	Copra
Balsam	Hops	Petroleum
Bullion	Enamel ware	Rum
Hides	Metal leaf	Sugar
Indigo	Paints	BRITISH WEST INDIES—420-422
Rubber	Paper	Aloes
Sugar	Porcelain	Balata
CEYLON—169	Soapstone	Gold
Rubber	Lithographic stone	Melasses
Cocoanut oil	Tin foil	Sugar
Plumbago	Copper foil	Hides
Citronella oil	Steel wire	Citrate of lime
	Brass wire	Lime oil



## BOOK REVIEWS

**Industrial Chemistry for Engineering Students.** By HENRY K. BENSON, PH.D., Professor of Industrial Chemistry in the University of Washington. New York: The Macmillan Company. 1913. About 12mo., xiv + 431 pages. Price, \$1.90.

In the words of the author, "The purpose of this text is to describe from the standpoint of chemistry, the most common materials used in the various branches of engineering. Emphasis is accordingly laid upon the occurrence, the mode of manufacture, the properties, and, to a limited extent, the uses of the various materials." It is stated to be "an elaboration of the author's lecture notes used during the last eight years in the courses of industrial chemistry for second year engineering students." The book includes the following chapters: General Processes and Apparatus; The Atmosphere; Industrial Water; Combustion and Destructive Distillation; Solid Fuels; Liquid and Gaseous Fuels; Petroleum and Lubricating Oils; Manufacture of Pig Iron; Commercial Forms of Iron and Steel; Industrial Alloys; Clay Products; Hydraulic Cements and Lime Products; Paving Materials and Wood Preservation; Paint and Varnish Materials; Plastics for Electrical Insulation; Cellulose Products; Explosive Materials.

Books of this kind will be in demand before long in engineering and technical schools as the increasing importance of the chemistry of engineering materials and operations, and the fact that many of their problems are essentially chemical ones, become impressed upon our engineers. Few engineering schools as yet have devoted time specifically to this purpose, very justly feeling that the inexperience of chemistry professors in engineering matters would seriously discount the value of the instruction. Such attention to the matter as is unavoidable is usually given in connection with specific engineering subjects by the engineer in charge. This treatment is succinct—a great advantage to the student, for while some engineers are reasonably good chemists, yet the average chemical intelligence of even engineering teachers is often pathetic to the same degree as is the engineering intelligence of chemistry teachers.

While not strictly the first, Dr. Benson is one chemist who has had the courage and the industry to attempt to be of service in this field. One might take exception perhaps to the calling of such a course as covered by this book, *Industrial Chemistry*, when it professes to be a course in the chemistry of engineering materials. The words *Industrial Chemistry* can doubtless be applied to such work, though many of us, I believe, would prefer that it be confined as is generally done, to the study of the chemical and engineering problems involved in the manufacture of chemical substances or the solution of industrial manufacturing problems by chemical means or operations, a matter not exactly germane to the training of civil or electrical engineers, for example. From the point of view of the author's expressed purpose the work in question should be called *Engineering Chemistry* or the *Chemistry of Engineering (Materials)*. The author was doubtless hampered by the fact that his college catalogue labeled his course *Industrial Chemistry* instead of *Engineering Chemistry* and, therefore, it is to be expected that this confusion would be difficult to repress in the book itself and an attempt made to cover both fields. The book lives up more closely to its title than to its purpose. It really is a series of chapters from *Industrial Chemistry* and, therefore, contains much material which has little general engineering interest though important to the industrial chemist or chemical engineer.

In commenting specifically upon the treatment of the different topics in the book the reviewer is attracted to those portions with which he is more familiar or with whose leaders he has had the most contact,

By "Charcoal Retorts," on p. 95, probably is meant the modern oven plants which with two exceptions in the U. S. are rectangular in shape. The common retort plants, of which there are still above twenty-five in the U. S., use cylindrical retorts exclusively but this type uses a retort of less than a cord capacity and never uses cars in the retort in this country. The statement that "acetic acid (2%) and "methyl alcohol (7%)" is obtained from hardwood is not commercial experience. It may be the figures were intended to have been reversed. Vacuum evaporators are not yet a success on acetate of lime in this country, nor is *brown acetate* of lime made from redistilled pyroigneous acid. The product is gray acetate. Neither is the dried acetate of lime "usually . . . . moderately heated to volatilize the tarry matter which separates," etc. It is scarcely proper to say acetate of lime "is almost completely utilized in the manufacture of acetic acid" without intimating that our acetone supply comes from the destructive distillation of this same acetate of lime.

The obvious necessity for brevity has at times led the author into a position open to serious misinterpretation. For instance, the statement that the Semet Solvay and Otto Hoffman ovens "are identical in principle, the main difference being in the arrangement of the flues for the combustion of the gases used in heating them," hardly represents the facts. Then a few lines further both types are covered in a joint description, most of which deals with their *regenerative checker work systems*. This faces a full page illustration of sections through the Semet-Solvay type very properly showing no regenerative checker work whatever.

One wonders why students must be introduced solely to the German method of distilling Coal Tar, when American practice is so admirably and thoroughly handled by one who knows, in Rogers and Aubert's "Industrial Chemistry" in the Chapter by F. E. Dodge. This account—the best ever written—is not even cited.

In such a brief treatment of the clay-products, nine pages devoted to a classification of clays which is largely geological seems excessive even if it has the merit of being the hitherto unpublished work of an eminent authority (Dean Edward Orton, Jr.). The rational analysis of clay is given large space in proportion to its standing. Crushing strength, as well as the tensile strength mentioned, is used as a measure of cohesive strength of clays. Air shrinkage in drying clay products should have been given as running from two to fifteen per cent, averaging about five per cent. Quartz should have been included in the list specific gravities of clay constituents. The Citation: "The Uses of Hydraulic Cements," p. 310, is by Eno and not Bleininger as given.

Cold curing of rubber is stated to be accomplished by treating a *solution* of rubber in carbon disulfide with sulfur monochloride, instead of treating the uncured or the compounded rubber with sulfur monochloride dissolved in carbon disulfide, etc. The description of "ethyl alcohol from sawdust" hardly leaves one sufficiently impressed with the fact that this industry is still in the "prospect" stage.

As may be seen from the list of chapters already mentioned the topics treated in the book are well selected from an engineering point of view. The illustrations are usually very good and for the most part quite modern and refreshing. The excellent bibliography at the end of each chapter is a very commendable feature of the book.

JAMES R. WITHEROW

**Metallurgy of Copper.** By H. O. HOFMAN. 8vo. 556 pp. McGraw-Hill Book Company, New York. Price, \$5.00.

In his "General Metallurgy" Dr. Hofman promised to supplement it with special volumes dealing with the principal metals,

and has issued this, the first of them, with commendable promptness. The "Metallurgy of Copper" is a worthy successor to the other book and will prove of much value and interest, not only to copper smelters but to those engaged in other branches of metallurgy.

The introduction is followed by short, but sufficient, chapters on "Commercial Copper, Its Impurities and Their Effects," "Alloys," "Compounds" and "Ores." After this, the various smelting processes for sulfide ores are taken up in order—Roasting, Blast Furnace Smelting, Reverberatory Smelting, The Converter. In each case the necessary apparatus is fully described and well illustrated from current practice—from American practice wherever possible. The variations under different conditions are pointed out and the reasons for them explained, with their advantages and disadvantages. The conduct and theory of the operations are fully given and in such a manner that theory and practice go hand in hand.

The smelting of native copper and of oxidized ores are then described in the same thorough manner. This is followed by an excellent chapter on refining.

The next section of the work deals with hydrometallurgy, giving the methods that have been proposed and tried for ores, matte and metal. While many of the processes described have not succeeded, they are of interest and value. In many cases they are the basis of experiments now being undertaken with a better chance of success, owing to changed commercial conditions and the better means now available for handling large quantities of ores and solutions. In this, as in the earlier chapters, the descriptions are clear and full, and the amount of information given is very large.

The last chapter deals with Electrolysis, and describes the principles and process clearly and well, giving good descriptions of plants using each of the modifications of the process.

One of the most valuable features of this, as of his previous book, is the copious bibliography and its convenient arrangement as foot-notes to each page. The proof-reading has been better, and there are fewer errors due to carelessness in this respect. The paper and binding, unfortunately, are no improvement on the "General Metallurgy." Altogether, Dr. Hofman has produced an excellent book which can be heartily recommended to all interested in the subject.

GEORGE C. STONE

**Fixation of Atmospheric Nitrogen.** By JOSEPH KNOX, D.Sc., Lecturer on Inorganic Chemistry, University of Aberdeen. Published by D. Van Nostrand Company. Price, 75 cents.

The book is divided into three sections: Section I deals with the conversion of atmospheric nitrogen into nitric and nitrous acids and their salts. The first part briefly describes the physico-chemical researches made in order to determine: whether the reaction is thermal or electrical; the best yield of nitric acid in the arc; the processes for the absorption of the acids; etc. The second part describes the most important processes in existence for the technical manufacture of nitrates and nitrites.

Section II takes up the synthesis of ammonia and ammonium compounds from atmospheric nitrogen. A short description of the Haber process is given with the data obtained from the experimental furnace. The technical manufacture of ammonia is not described.

Section III discusses the conversion of atmospheric nitrogen into compounds which readily yield ammonia. The various nitrides are mentioned. Serpek's aluminum nitride and the calcium cyanamide processes are discussed, both from the scientific and technical aspects.

The bibliography given at the end of the book is fairly complete, and deserves attention.

Owing to the fact that the subject matter of this chemical

monograph is very extensive, one cannot expect the author to cover his subject in 102 pp. with any degree of thoroughness. The book may be recommended to those who wish to get a bird's-eye view of the subject of Fixation of Atmospheric Nitrogen, from the scientific as well as from the commercial point of view.

ALEXANDER LOWY

**Neues Handbuch der Chemischen Technologie.** Published by Friedr. Vieweg & Sohn in Braunschweig. Editor-in-Chief, Prof. Dr. C. Engler, Karlsruhe, Germany.

There are seven volumes in this "handbook" series, which, like the following three volumes, can be considered as separate books and bought as such. While this series is intended as a third edition of Bolley's "Handbuch der Chemischen Technologie," so many changes have been made in revising and modernizing the older editions that an entirely new title has been selected.

Vols. I and II. **The Coal-tar and Ammonia Industry.** By DR. GEORGE LUNGE AND DR. HIPPOLYT KÖHLER. Vol. I, *Steinkohlenteer*, 928 pp., and 354 illus. Price, 30 Marks.

This volume is divided into ten chapters as follows: 1—Coal as Raw Material of Coal-tar. 2—Sources of Tars for Raw Material in the Coal-tar Industry. 3—Properties of Coal-tar and of Its Constituent Parts. 4—Uses of Coal-tar without Distillation. 5—The First Distillation of Tar. 6—Pitch. 7—Anthracene Oil. 8—Heavy Oil. 9—Second Light Oils (phenol, cresole and naphthalene). 10—Light Oils. The book is clearly printed on a very good quality of paper and is profusely illustrated throughout. A great deal of attention is given to the mechanical side of the coal-tar industry, and while most of the illustrations are line drawings, in some cases actual photographs have been used, thus showing clearly the construction and operation of most of the apparatus used. The chemical side of the industry is equally well presented, and many tables of physical constants are given. There are also numerous references to the literature and patents. This book is very complete and should prove of great value to those chemists interested in coal-tar and should be in every reference library.

Vol. II, *Ammonia*. 462 pp. 163 illus. Price, 16 Marks.

There are eight chapters: 1—History of Ammonia; Development and Future of the Ammonia Industry. 2—Properties of Ammonia and Its Technically Prepared Salts. 3—Natural Occurrences of Ammonia and Suggestions for Its Industrial Manipulation. 4—Composition and Analysis of Ammonia Water. 5—Manufacture of Ammonia Water. 6—Production of Spirits of Ammonia and Liquid Ammonia. 7—Production of Ammonium Sulfate from Ammonia Water. 8—Manufacture of Other Technically Important Ammonium Salts (Chloride, Fluoride, Ferrocyanide, Sulfocyanide, Carbonate, Nitrate, Nitrite, Persulfate, Perchlorate, Thiosulfate, Phosphate, Chromate, Formate, Acetate, Oxalate). The many advances and improvements in the manufacture of illuminating gas and the production of coke, especially the by-products, fully justify this new edition, which, like Vol. I, should prove a valuable reference book.

Vol. V. **Manufacture of Lamp Black and Charcoal.** By HIPPOLYT KÖHLER. 221 pp. 114 illus. Price, 8 Marks.

This, the third edition, is about the only book published which thoroughly covers the manufacture and uses of lamp black and charcoal. Dr. Köhler has brought this edition up to date and has paid considerable attention to the uses of charcoal as a decolorizing agent. The book is even more fully illustrated than Vols. I and II, and contains, as well, many analyses and valuable tables. It is divided into four chapters: 1—General Information of the Properties and Uses of Carbon. 2—Lamp Black. 3—Charcoal. 4—Examination and Investigation of Lamp Black and Charcoal.

This series of valuable books would be of even greater interest and value to American chemists and students if they were translated into English. German fashion, they are published in both

cloth and paper bindings, the paper binding being about 25 cents cheaper. The "Neues Handbuch" series should be well bound and on the shelves of all chemical libraries.

ROBERT K. MURPHY

**Examination of Lubricating Oils.** By THOS. B. STILLMAN, M.Sc., Ph.D. Easton, Pa.: The Chemical Publishing Co., 1914. 125 pp. Price, \$1.25.

The descriptions of the determination of specific gravity and cold test are very full and complete. For the determination of viscosity, among other instruments, the Saybolt "A" viscosimeter is described. His universal which has replaced the A, B, and C forms is not mentioned. The statement that "Tagliabue's Viscosimeter is used to a very large extent by the manufacturers of lubricating oils in the United States" would seem to be open to question as are also the readings obtained with it.

In the description of the flash test, the Abel tester for *burning oils* is given, and the apparatus perhaps most extensively used in this country for lubricating oils—the Cleveland Tester—barely noticed.

The book contains a number of tables, pp. 10, 12, 35, and 51. It would have economized space and detracted nothing from the use of the work to have condensed these into one, and it would have saved time for the user had the oils there given been arranged alphabetically. These tables are from results obtained in the author's laboratory; while they are valuable as showing American conditions, yet it would seem to have been advisable to have included as well the limits of the usual characteristics found. For example, the iodine number of neat'sfoot oil is given as 80–82; inasmuch as the highest figures usually reported are 72–76, it would seem as if these samples were suspicious.

The directions for the valuable Maumené and Iodine tests are very incomplete, the precautions necessary for their successful use not being fully given.

Nearly two pages are devoted to color tests for the different oils, notwithstanding the fact that they are notoriously unreliable; strangely enough the best one of them all—The Halphen test for cottonseed—is omitted. The method for the separation of mineral from the organic oils leaves something to be desired as the ethyl ether used dissolves some of the soap formed.

The references to the Proceedings of the American Society of Testing Materials, pp. 48, 60–65, are not clearly given, and in some cases material has been taken from this source without it being so indicated. Nor is the selection of testing machines a particularly happy one, those considered the best not being clearly mentioned.

The chapter on specifications for the various oils used by the various railroads, cities, and the federal government will be found valuable, as will also the procedure for the analysis and synthesis of cylinder oils, and the analysis of cylinder deposits.

A. H. GILL

**Laboratory Course in Electrochemistry.** By OLIVER P. WATTS, Ph.D. New York: McGraw-Hill Book Company. 150 pp. Price, \$1.00.

There are several books at present both in English and German dealing with this subject, but this manual by Dr. Watts is of special interest, as it evidently follows the work in applied electrochemistry as it is conducted at the University of Wisconsin.

The book deals with electrochemistry in aqueous solution and does not touch on the subject of the electric furnace either for thermic or electrolytic purposes. Beginning with a short description of suitable equipment and very excellent advice to the student, there is given a list of experiments covering Faraday's law, resistivity of electrolytes, electromotive force, discharge potentials, passive state corrosion, separation and plating of metals and electrolytic preparations. Particular attention is

given to the subject of electroplating and the treatment is excellent.

It would have been better to have had more sketches or diagrams in some of the experiments described as it would enable the student to grasp the meaning more quickly.

Comparatively little attention is given to the electrolytic separation of metals as it is recognized that this subject is treated very fully in other books on the subject.

An excellent feature of the book is in giving references as each subject is taken up.

Organic preparations are not touched on and the inorganic preparations are mostly taken from the several books dealing with this subject.

The appendix includes some useful tables and one of particular interest—giving the approximate potentials of the metals in various electrolytes as the data were obtained by the students in their regular work in the University.

The book will be found very helpful in the laboratory teaching of applied electrochemistry.

SAMUEL A. TUCKER

**Chemistry of Rubber.** By B. D. PORRITT, B.Sc., F.I.C., Chief Chemist to the North British Rubber Company and published by D. Van Nostrand Company, New York City, 1913; one of a series of Chemical Monographs edited by A. C. Cumming. Price, \$0.50.

The book contains 93 pages of subject matter. It is an admirable, briefly written review of the status of rubber chemistry up to the time it was printed. The author is to be commended for excellent English, brevity of expression and freedom from unduly emphasizing or advocating theories upon which there are several dissimilar points of view. It contains the following divisions:

I—The Properties of Crude Rubber. II—Constitution and Derivatives. III—Methods of Vulcanization. IV—Theories of Vulcanization. V—Waste Rubber and Its Utilization. VI—Synthetic Caoutchouc.

These are followed by a bibliography of the published work referred to in the body of the text and a brief index.

The book is an excellent one for students and for those who wish a brief statement of the essentials of rubber chemistry.

W. C. GEER

**A Chart of the Carbon Compounds.** Prepared by CHARLES W. CUNO, A.M. Published by the Department of Efficiency, University of Denver, University Park, Colo. Size, 31½ × 43½ in. Price, postage paid, \$0.30.

"The chart is designed for student use in Organic Chemistry, but may also be of value to chemists in organic work." It gives the divisions of organic compounds, such as hydrocarbons, halogen derivatives, alcohols, etc., in the horizontal rows and the different classes under each divisional heading in the vertical rows. This arrangement brings both aliphatic and aromatic compounds in the same general division and is very good. In each case are usually given the general formula, structure, methods of synthesis, and chemical properties as shown by reactions. The chart is printed plainly and is generally well arranged. Some of the structural formulas, however, are awkward, and it is unfortunate that there should be so many typographical errors in structural and empirical formulas and in the names of compounds. There are a number of statements which are misleading, and there are some to which many chemists would take exception. The chemistry is that of the text-books of a number of years ago. There is no mention of the important Grignard methods and of the many applications of metals and of catalytic reductions in syntheses.

A chart visualizes and correlates facts and relationships and therefore it will always be of service.

HARRY L. FISHER



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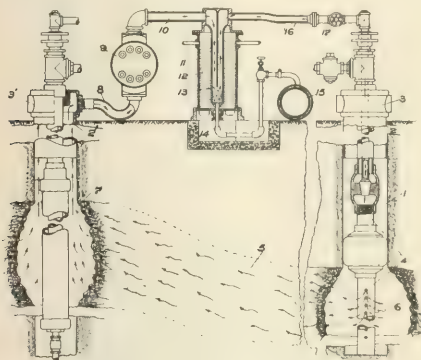
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## RECENT INVENTIONS

By C. L. PARKER, Solicitor of Chemical Patents, McGill Building, Washington, D. C.

**Ferment.** P. Altenfeld, August 4, 1914. U. S. Pat. 1,105,601. A dough is formed of malt, rye, corn-flakes and water and allowed to ferment at a relatively low temperature.

**Gasoline.** J. W. Waitz, August 4, 1914. U. S. Pat. 1,105,727. This process is designed for the production of the lighter hydrocarbon liquids, and vapors, notably gasoline, from the older developed territories where the natural gas pressure is reduced to such an extent that such hydrocarbons will not flow spontaneously from the wells which have been drilled into the pro-



ducing strata or where the supply of such hydrocarbons has been almost exhausted. Air or gas under pressure is passed at a comparatively low temperature through a stratum in which hydrocarbon fluids are contained; the resulting saturated air or gas is then put through a condenser to separate the desired hydrocarbons.

**Refining Vegetable and Animal Oils.** C. Baskerville, August 4, 1914. U. S. Pat. 1,105,744. The oil is agitated with fibrous vegetable material impregnated with an alkali, the fibrous material and contained impurities being later filtered out.

**Gas from Oil.** W. A. Hall, August 4, 1914. U. S. Pat. 1,105,772. A combustible gas is produced by subjecting a mixture of mineral oil and water to the action of metallic nickel at a temperature of about 650° to 750° C.

**Stannic Chlorid from Materials Containing Tin Oxid.** H. Goldschmidt, August 4, 1914. U. S. Pat. 1,105,902. Oxid of tin is reduced under conditions to produce a porous mass containing the tin in a metallic state and this mass is subjected to the action of chlorin gas.

**Gasoline from Fuel Oil.** W. M. Burton, August 4, 1914. U. S. Pat. 1,105,961. Fuel oil or other products of petroleum distillation having a boiling point of upward of 500° F. is distilled at a temperature of from about 650° F. to about 850° F., the volatile constituents of the liquid being conducted off and condensed under a pressure of from about 4 to 5 atmospheres. The volatile constituents of the residue are then distilled off under approximately atmospheric pressure. The product of the last condensation is then re-subjected to the first treatment.

**Isoprene.** Earle and Kyriakides, August 5, 1914. U. S. Pat. 1,106,290. The vapors of methylisopropylketone are passed over heated aluminum silicate and the isoprene is separated from the other products of the reaction.

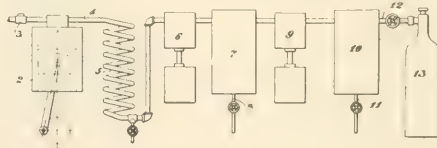
**White Lead.** E. Euston, August 11, 1914. U. S. Pat. 1,106,793. The composition is produced by the admixture of a precipitate formed by carbon dioxide gas from a basic lead acetate solution eventually approximately neutral with a precipitate formed by carbon dioxide gas from basic lead acetate solution eventually acid. The admixture is made in proportions to form a pigment containing 11.0 per cent to 14.5 per cent carbon dioxide.

**Argon and Rare Atmospheric Gases.** J. E. Bucher, August 11, 1914. U. S. Pat. 1,106,921. Argon and incidentally the other rare inert atmospheric gases helium, xenon, krypton, and neon are separated from atmospheric nitrogen by passing such nitrogen, free from oxygen, over a heated reactive mass containing finely divided catalytic material (preferably iron filings), associated with carbon and free alkali metal (preferably sodium) and collecting the gaseous residues of the reaction.

**Potassium Compounds from Silicious Materials.** T. B. Stillman, August 11, 1914. U. S. Pat. 1,106,984. The potash-bearing silicious material is ground, mixed with a sufficient quantity of carbonate of potash to convert all of the silica present into potassium silicate and the mixture fused at a high temperature. The fusion is ground and the potassium aluminate and potassium oxid are extracted with cold water. The solution is made more alkaline and then sufficient ammonium salt to precipitate all of the alumina in the aluminate of potash as hydrated aluminum oxid; the liquor is then separated from the precipitate and charged with a sufficient carbonic acid to convert the potassium hydroxide to carbonate of potash. The solution is then evaporated and the potash recovered from the cold-water-insoluble residue.

**Tanning Compound.** L. Pollak, August 11, 1914. U. S. Pat. 1,107,107. The composition is produced by condensing phenol, sulfuric acid and grape sugar.

**Carbon Monoxid, Hydrogen, and Nitrogen.** Brownlee and Uhlinger, August 18, 1914. U. S. Pat. 1,107,581. Carbonaceous material, preferably gas or gasoline vapor, is mixed with an amount of air sufficient to support incomplete combustion of the mixture to produce a maximum amount of carbon monoxid and hydrogen and the mixture is exploded preferably in an



internal combustion engine. The carbon monoxid, hydrogen and nitrogen are then separated from the exhaust gases. The products of combustion, water vapor, carbon dioxide, carbon monoxid, hydrogen and nitrogen pass through the exhaust pipe 4 to a refrigerating coil, 5, where the gases are cooled and the moisture separated as water, thence to compressor 6 where the gases are compressed and the carbon dioxide is liquefied and collected in the holder 7. The hydrogen, carbon monoxid and nitrogen pass to a compressor, 9, where the gases are further compressed and the carbon monoxid and nitrogen are liquefied and collected in a holder, 10. The remaining hydrogen passes through outlet 12 to a receiver or holder, 13.

**Ethane.** Mulliken and Moore, August 18, 1914. U. S. Pat. 1,107,696. In this process exothermic compounds, such as ethane,

are produced from endothermic compounds, such as ethylene or acetylene, by subjecting the latter in the presence of a re-

Pat. 1,110,819. Pure turpentine is obtained from impure turpentine by drawing through it air warmed to a temperature of not substantially above  $212^{\circ}\text{F}$ . and condensing the vapors drawn off with the air.

**Treating Heavy Hydrocarbon Oils.** C. J. Greenstreet, Sept. 15, 1914. U. S. Pat. 1,110,923. Crude oil is converted into light hydrocarbons, liquid at ordinary atmospheric temperatures, by atomizing the crude oil with steam and passing the mixture continuously through a pipe system maintained at a substantially cherry-red heat. A portion of the hot product is ignited and the proportion of crude oil and steam varied so that the flame burns without smoking. The remaining product is condensed.

**Methyl Chlorid.** B. S. Lacy, Sept. 29, 1914. U. S. Pat. 1,111,842. Methyl chlorid is produced by reacting upon chlorine gas with a proportion of methane greater than the theoretical one.

**Wood Distillation.** M. C. Whitaker, Sept. 15, 1914. U. S. Pat. 1,110,850. Wood or other material to be subjected to distillation is spaced away from the walls of the retort and the

ducing agent to catalytic action and simultaneously refrigerating the product to extract the heat liberated by the reaction.

**Boric Acid.** A. Burger, August 25, 1914. U. S. Pat. 1,108,129. Boric acid is produced by calcining a borate and heating the resulting products with carbon dioxide in the presence of water.

**Water-Repellent Cement.** C. Ellis, Sept. 1, 1914. U. S. Pat. 1,109,120. Waterproof concrete is produced by mixing with the cementitious material a composition containing mineral oil, a water-soluble soap in solution and a water-insoluble soap.

**Refining Petroleum and Its By-Products.** E. A. Starke, Sept. 1, 1914. U. S. Pat. 1,109,187. Aromatic hydrocarbons are separated from petroleum by adding sulfuric acid and subjecting the mixture to agitation in a closed vessel in the presence of heat until the specific gravity of the oil becomes constant and no longer decreases upon the addition of sulfuric acid. The sulfur dioxide produced by the reaction is not allowed to escape but is retained by the oil from which it is later separated by blowing in air or steam. The treated oil is allowed to settle until the sulfonic acids have separated from the petroleum and are drawn off.

**Stable Hydrogen Peroxid.** A. Schaidhauf, Sept. 8, 1914. U. S. Pat. 1,109,791. A neutral solution of hydrogen peroxid is rendered stable by the addition of soap.

**Softening Water.** H. Ley, Sept. 8, 1914. U. S. Pat. 1,109,849. The water is treated with a precipitate obtained by mixing a solution of phosphate of soda with a solution of an alkali-metal silicate.

**Varnish Manufacture.** S. E. Ford, Sept. 8, 1914. U. S. Pat. 1,109,979. The oxidizable varnish-forming liquid is confined in the chamber 10 under oxidizing conditions, preferably in contact with ozone, and heated and agitated to reduce it to a fine spray.

**Formaldehyde.** H. von Hochstetter, Sept. 8, 1914. U. S. Pat. 1,110,289. A mixture of methyl alcohol vapor and air is conducted over metallic silver with which metallic rhodium is associated, the vapor mixture being caused to contact with the metals at an elevated temperature.

**Aluminum Fluorid.** C. A. Doremus, Sept. 15, 1914. U. S. Pat. 1,110,675. Aluminum fluorid having variable amounts of water of crystallization (or none) is obtained by heating in a closed vessel a solution of aluminum fluorid, the proportion of water of crystallization diminishing as the temperature applied is raised.

**Pure Turpentine.** T. W. Pritchard, Sept. 15, 1914. U. S.

temperature of the contents of the retort equalized by the agitation of the gases and vapors within.

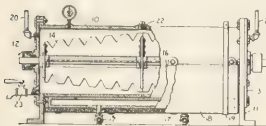
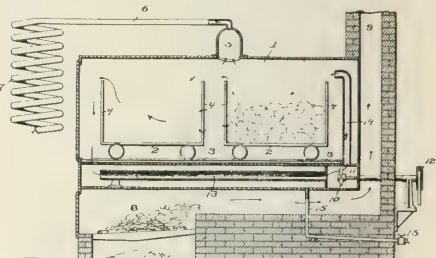
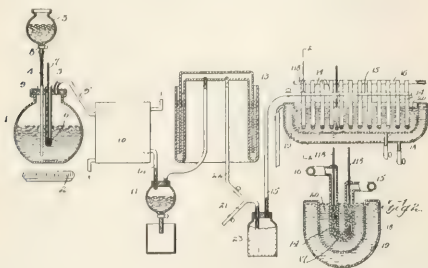
By regulating the heat applied to the retort and at the same time circulating the gases and vapors about the charge, it may be brought to any temperature desired and held there so as to effectively drive off all of any substance vaporizable at that temperature.

**Copper Ores.** C. S. Vadner, Sept. 29, 1914. U. S. Pat. 1,111,874. Sulfid ores of copper naturally oxidized and sufficiently roasted are dissolved in a solution of sodium chlorid saturated with sulfur dioxide gas in the presence of heat. The excess of sulfur dioxide gas is blown out and the copper precipitated as a basic copper carbonate by adding finely pulverized calcium carbonate to the cold solution and passing air through it.

**Alkali-Silico Aluminate Richer in Alkali than Feldspar.** A. H. Cowles, Sept. 29, 1914. U. S. Pat. 1,111,881. A mixture of clay, carbon and salt is formed into small masses and subjected in a rotary furnace to the action of water vapor and furnace combustion gas.

**Wax from Other Hydrocarbons.** W. M. Burton, Sept. 29, 1914. U. S. Pat. 1,112,113. A wax-free hydrocarbon of a high boiling point is distilled under a pressure of about four atmospheres and at a temperature of about  $650^{\circ}\text{F}$ . The residuum of this distillation is then distilled at a low pressure. The distillate of the second distillation is then chilled and the paraffin wax pressed out from it.

**Phosphoric Acid.** I. Hechenbleikner, Sept. 29, 1914. U. S. Pat. 1,112,211. Natural phosphate rock mixed with silicious material and carbon is heated to produce vapors of phosphorus. The furnace gases and vapors are withdrawn in a stream which is broken up and mixed with oxygen. The resulting acid is absorbed by water in towers operated on a countercurrent system.





# MARKET REPORT

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR THE MONTH OF NOVEMBER, 1914

## ORGANIC CHEMICALS

Acetanilid.....	Lb.	34	@	—
Acetic Acid (28 per cent.).....	C.	1 75	@	1 90
Acetone (drums).....	Lb.	16	@	—
Alcohol, denatured (180 proof).....	Gal.	34	@	35
Alcohol, grain (188 proof).....	Gal.	2 60	@	2 65
Alcohol, wood (95 per cent.).....	Gal.	48	@	47
Amyl Acetate.....	Gal.	2 75	@	—
Aniline Oil.....	Lb.	80	@	60
Benzoic Acid.....	Lb.	60	@	70
Benzol (90 per cent.).....	Gal.	34	@	35
Camphor (refined in bulk).....	Lb.	88	@	—
Carbolic Acid (drums).....	Lb.	30	@	—
Carbon Bisulfide.....	Lb.	3 4	@	10
Carbon Tetrachloride (drums).....	Lb.	12	@	—
Chloroform.....	Lb.	9	@	35
Citric Acid (domestic), crystals.....	Lb.	68	@	67
Dextrine (corn).....	C.	5 8	@	5 12
Dextrine (imported potato).....	Lb.	—	@	—
Ether (U. S. P., 1900).....	Lb.	18	@	20
Formaldehyde.....	Lb.	8 1 2	@	9 1 2
Glycerine (dynamite).....	Lb.	2 1 2	@	25
Oxalic Acid.....	Lb.	1 2	@	18
Pyrogalllic Acid (bulk).....	Lb.	1 90	@	2 10
Salicylic Acid.....	Lb.	70	@	75
Starch (cassava).....	Lb.	3 1 2	@	4
Starch (corn).....	C.	2 09	@	30
Starch (potato).....	Lb.	68	@	—
Starch (rice).....	Lb.	60	@	—
Starch (sago).....	Lb.	60	@	—
Starch (wheat).....	Lb.	5	@	10
Tannic Acid (commercial).....	Lb.	60	@	66
Tartaric Acid, crystals.....	Lb.	1 1 1 2	@	46

## INORGANIC CHEMICALS

Acetate of Lead (brown, broken).....	Lb.	7 4	@	7 1 4
Acetate of Lime (gray).....	C.	1 75	@	1 90
Alum (lump).....	C.	1 75	@	3 00
Aluminum Sulfate (high grade).....	C.	1 50	@	2 00
Ammonium Carbonate (domestic).....	Lb.	9	@	10
Ammonium Chloride, (gray).....	Lb.	6 4	@	6 1 4
Aqua Ammonia (drums) 16°.....	Lb.	29 1 4	@	2 1 2
Arsenic (white).....	Lb.	4 1 2	@	6
Barium Chloride.....	Ton	75 00	@	90 00
Barium Nitrate.....	Lb.	15	@	16
Barytes (prime white, foreign).....	Ton	30 00	@	27 00
Bleaching Powder (35 per cent).....	C.	1 75	@	2 50
Blue Vitriol.....	C.	4 35	@	4 55
Borax, crystals (bags).....	Lb.	4 1 4	@	1 4
Boric Acid, crystals (powd.).....	Lb.	7 4	@	80
Brimstone (crude, domestic).....	Long Ton	22 00	@	22 50
Bromine (bulk).....	Lb.	40	@	50
Calcium Chloride (lump).....	Ton	11 10	@	1 00
Chalk (light precipitated).....	Lb.	5	@	6
China Clay (imported).....	Ton	14 00	@	16 00
Feldspar.....	Ton	8 00	@	14 00
Fuller's Earth (powdered, foreign).....	Ton	—	@	—
Green Vitriol (bulk).....	C.	58	@	60
Hydrochloric Acid (18°).....	C.	1 15	@	1 65
Iodine (resublimed).....	Lb.	3 75	@	4 00
Lead Nitrate.....	Lb.	8 1 4	@	8 1 4
Litharge (American).....	Lb.	5	@	5 1 4
Lithium Carbonate.....	Lb.	1 00	@	1 10
Magnesium Carbonate.....	Lb.	4 1 4	@	6
Magnesite "Calcined".....	Ton	40 00	@	50 00
Nitric Acid (36°).....	Lb.	37 1 4	@	4 1 4
Phosphoric Acid (sp. gr. 1.75).....	Lb.	28	@	28 1 2
Phosphorus.....	Lb.	38	@	98
Plaster of Paris.....	Bbl.	1 50	@	1 50
Potassium Bichromate.....	Lb.	12	@	14
Potassium Bromide.....	Lb.	70	@	80
Potassium Carbonate (calcined), 80 @ 85%.....	C.	1 3	@	18
Potassium Chlorate, crystals.....	Lb.	50	@	50
Potassium Cyanide (bulk), 98-99%.....	Lb.	58	@	30
Potassium Hydroxide.....	C.	32 00	@	10 00
Potassium Iodide (bulk).....	Lb.	3 15	@	3 25
Potassium Nitrate (crude).....	Lb.	—	@	—
Potassium Permanganate (bulk).....	Lb.	50	@	—
Quicksilver, Flask (75 lbs.).....	50 00	@	55 00	
Red Lead (American).....	Lb.	5	@	6
Salt Cake (glass makers').....	C.	28	@	68
Silver Nitrate.....	Oz.	31	@	38

Soapstone in bags.....	Ton	10 00	@	12 00
Soda Ash (48 per cent.).....	C.	65 1 2	@	7 1 2
Sodium Acetate.....	Lb.	5	@	7
Sodium Bicarbonate (domestic).....	C.	1 00	@	1 10
Sodium Bicarbonate (English).....	Lb.	3 1 2	@	4
Sodium Bichromate.....	Lb.	4 1 4	@	5
Sodium Carbonate (dry).....	C.	60	@	80
Sodium Chlorate.....	Lb.	16	@	18
Sodium Hydroxide (60 per cent).....	C.	1 55	@	1 57 1 2
Sodium Hyposulfite.....	C.	1 60	@	1 50
Sodium Nitrate (95 per cent, spot).....	C.	1 85	@	1 90
Sodium Silicate (liquid).....	C.	60	@	70
Strontium Nitrate.....	Lb.	1 1	@	17
Sulfur, Flowers (sublimed).....	C.	1 10	@	2 60
Sulfur, Roll.....	C.	1 80	@	2 15
Sulfuric Acid (60° B).....	C.	80	@	1 00
Talc (American).....	Ton	15 00	@	20 00
Terra Alba (American), No. 1.....	C.	75	@	80
Tin Bichloride (50°).....	Lb.	9 1 2	@	10
Tin Oxide.....	Lb.	38	@	40
White Lead (American, dry).....	Lb.	5	@	5 1 4
Zinc Carbonate.....	Lb.	8 1 2	@	9
Zinc Chloride (granulated).....	Lb.	45	@	50
Zinc Oxide (American process).....	Lb.	5 1 4	@	6 1 2
Zinc Sulfate.....	C.	2 35	@	2 70

## OILS, WAXES, ETC.

Beeswax (pure white).....	Lb.	48	@	52
Black Mineral Oil, 29 gravity.....	Gal.	3 4 1 2	@	14
Castor Oil (No. 3).....	Lb.	8 1 4	@	9
Ceresin (yellow).....	Lb.	12	@	22
Corn Oil.....	C.	5 35	@	5 45
Cottonseed Oil (crude), f. o. b. mill.....	Gal.	3 1 2	@	3 1 2
Cottonseed Oil (p. s. y.).....	Lb.	5 1 4	@	6
Cylinder Oil (light, filtered).....	Gal.	3 1 2	@	3 2
Japan Wax.....	Lb.	12	@	13
Lard Oil (prime winter).....	Gal.	90	@	92
Linseed Oil (raw).....	Gal.	46	@	48
Menhaden Oil (crude).....	Gal.	34	@	—
Naphtha, 68 @ 72°.....	drums	—	@	17
Neatsfoot Oil (20°).....	Gal.	90	@	98
Paraffine (crude, 120 & 122 m. p.).....	Lb.	3 1 4	@	3 1 4
Paraffine Oil (high viscosity).....	Gal.	27	@	28
Rosin ("F" grade) (280 lbs.).....	Bbl.	2 05	@	1 05
Rosin Oil (first run).....	Gal.	25	@	—
Shellac, T. N.....	Lb.	14	@	14 1 2
Spermaceti (cake).....	Lb.	8	@	80
Sperm Oil (bleached winter), 38°.....	Gal.	70	@	71
Spindle Oil, No. 200.....	Gal.	18	@	19
Stearic Acid (double-pressed).....	Lb.	9	@	11
Tallow (acidless).....	Gal.	64	@	66
Tar Oil (distilled).....	Gal.	50	@	51
Turpentine (spirits of).....	Gal.	48	@	49 1 2

## METALS

Aluminum (No. 1 ingots).....	Lb.	18 1 4	@	1
Antimony (Hallet's).....	Lb.	18 1 2	@	160
Bismuth (New York).....	Lb.	80	@	2 90
Bronze powder.....	Lb.	—	@	—
Copper (electrolytic).....	C.	12 07 1 2	@	12 1 2
Copper (lake).....	C.	12 12 1 4	@	12 25
Lead, N. Y.....	C.	—	@	1 90
Nickel.....	Lb.	—	@	—
Platinum (refined).....	Oz.	50 00	@	52 00
Silver.....	Oz.	—	@	49 1 4
Tin.....	C.	32 10	@	—
Zinc.....	C.	5 20	@	5 25

## FERTILIZER MATERIALS

Ammonium Sulfate.....	C.	1 55	@	2 62 1 2
Blood (dried).....	Unit	3 15	@	3 20
Bone, 4 1/2 and 50 (ground, raw).....	Ton	27 50	@	—
Calcium Cyanamid.....	Unit of Ammonia	2 30	@	2 85
Calcium Nitrate (Norwegian).....	C.	—	@	—
Castor meal.....	Unit	—	@	—
Fish Scrap (domestic, dried).....	Unit	3 00	@	10
Phosphate, acid (16 per cent bulk).....	Ton	7 50	@	—
Phosphate rock, f. o. b. mine.....	Ton	2 25	@	2 50
Florida land pebble (68 per cent).....	Ton	5 00	@	5 50
Tennessee (70-80 per cent).....	Ton	5 00	@	5 50
Potassium, "murrate," basis 80 per cent.....	Ton	—	@	nominal
Pyrites (furnace size, imported).....	Unit	13	@	—
Tankage (high-grade).....	Unit	3 15	@	10

# AUTHOR INDEX

## THE JOURNAL OF INDUSTRIAL AND ENGINEERING CHEMISTRY VOLUME VI, 1914

ADAMS, H. M. Commercial Paper and Its Assay	669	BRAGG, C. T. American Alcohol Insoluble Test for Shellac. Note on Committee Report published in 1913.	356
ADAMS, M. AND C. HILTON. Wood Distillation under Diminished Pressure.	378	BRÄUER, O. L. The Strength of Nitric Acid. Period of Extraction, and Ignition as Affecting the Gravimetric Determination of Phosphoric Acid in Soils.	1004
ADDICKS, W. R. Statistical and Volumetric Method for Lead.	398	BRÄUTLICH, C. A. AND A. B. PARLIN. Preliminary Note on Iron in Florida.	960
AMERICAN SOCIETY FOR TESTERS. MATERIALS. Standard Specifications for Purity of Raw Linseed Oil from North American Seed.	164	AND G. CRAWFORD. Iron in Tomatoes.	1001
AMES, J. W. AND E. W. GAITHER. Determination of Carbon in Soils and Soil Extracts.	561	BRECKENRIDGE, J. E. Chemistry an Important Factor in the Fertilizer Industry.	505
ANDERSON, A. A. On Presence of Furfural in Cider Vinegar.	214	BRIDGMAN, J. A. AND C. E. F. LINDSELL. New Method for Determination of Hydrocyanic Acid and the Alkali Cyanides.	554
Correction	241	BRIGHTON, T. B., C. B. BARDWELL, B. A. BERRYMAN AND K. D. KUHR. Hydrocarbons of Utah. Correction.	865
ANDERSON, G. F. AND C. H. JONES. Procedure for Separating Organic Ammoniates from the Mineral Portion of Commercial Fertilizers.	580	BRINHAUD, W. Apparatus for Determination of Fat by the Rose-Gottlieb Method.	324
ANDERSON, R. P. Modified Hempel Pipettes.	237	BROCK, F. P., L. V. REDMAN AND A. J. WEITH. Determination of Phenol in Presence of Hexamethylenetetramine and Formaldehyde.	308
AND C. J. ENGELDER. Absorption of Gasoline Vapor in Natural Gas by Fuming Sulfuric Acid.	989	Synthetic Resins, 3; Correction, 171; Note.	263
ARNY, H. V. AND H. H. SCHAFER. Ferric Alum. Estimation of Casein.	748	BROOKS, B. T. Note on Antiseptics.	958
BACHMANN, F. New Seal for the Prevention of Aeration in Deaerated Liquids.	764	AND R. F. BACON. Fluorescence of Petroleum Distillates.	623
BACON, R. F. Obituary—Robert Kennedy Duncan.	346	BROWN, I. H. AND D. J. PRICE. Explosibility of Grain Dusts.	934
AND B. F. BROOKS. Fluorescence of Petroleum Distillates.	623	Correction	1039
BAERLAND, L. H. Invention of Celluloid. Editorial.	904	BROWN, C. A. Chemistry of Cattle Feeding and Dairying, by J. A. Murkay. (Book Review).	789
Presentation Address. Morris Loeb Memorial.	904	Der Starkeucker, by Wichelhaus. (Book Review).	358
Some Aspects of Industrial Chemistry. Chandler Foundation Lecture—1914.	904	167. Purification of White Sugar Manufacture by Harloff. (Book Review).	526
Synthetic Resins. Note.	769	BURGESS, G. K. AND P. D. SALE. Thermoelectric Method for the Determination of the Purity of Platinum Ware.	452
BAILEY, C. Determination of Hardness in Natural Waters.	107	BURKOWSKI, H. Relation of Composition of Ash in Coal to Its Fusing Temperature.	694
BAILEY, E. G. Technical Gas and Fuel Analysis by A. H. White. (Book Review).	267	BURKE, C. E. AND C. C. SCALONE. On Oil of Black Sage.	804
BATLEY, E. H. S. Report of Platinum Test at University of Kansas.	518	BURRELL, G. A. AND G. G. OBERPFEIL. Determination of Hydrogen in Mixtures by Means of Colloidal Palladium.	992
BAILEY, H. S. A Convenient Form of Weighing Burette.	320	AND F. M. SEIBERT. Experiments with Small Animals and Carbon Monoxide.	241
BAILEY, L. H. Non-Uniformity of Drying Oven Temperatures.	497	BUSHONG, F. W. Notes on the Composition of Mid-Continental Petroleum.	888
BAIN, J. W. AND A. E. WIGLE. Studies on Filtration.	672	BUSWELL, A. M. Modified Apparatus for the Putrescibility Test.	325
BARDWELL, C. B., A. B. BERRYMAN, T. B. BRIGHTON AND K. D. KUHR. Hydrocarbons of Utah. Correction.	865	Underground Waters for Commercial Purposes, by F. L. Rector. (Book Review).	701
BARBARO, H. E. AND H. E. BISCHOP. Effect of Bread Wrapping on the Chemical Composition of the Loaf.	736	CADENHEAD, A. F. G. AND W. O. WALKER. Note on Precipitation of Lactalbumin in Cows' Milk.	573
BARRY, F. Chemistry and its Borderland, by A. W. Stewart. (Book Review).	873	CAIN, J. R. Determination of Carbon in Steel and Iron by the Inductio. Carbonization Titration.	465
BARLOW, L. E. Improved Method for the Determination of Nitrogen in Steel.	1012	CAMERON, F. K. Principles and Practice of Agricultural Analysis, Vol. III, by H. W. Wiley. (Book Review).	525
BARTOW, E. AND C. SCHOLL. Comparative Value of Calcium and Magnesium-Calcium Lime for Water Softening.	189	CAMPBELL, E. D. Synthetic Celite and Large Crystals of Tricalcium Phosphate.	706
BASSETT, L. R. Apparatus for Taking Dust and Bacteria Sample of Air.	238	CAMPBELL, W. Metallurgy, by C. H. Desch. (Book Review).	525
Factors Involved in Opening up the Field of Unused Elements.	182	CARPENTER, F. B. Fertilizer Chemistry Division Report, Cincinnati Meeting A. C. S.	513
Investigation of School Air in New York City. Address at Ventilation Symposium.	675	Principles of Agricultural Chemistry, by G. S. Fraps. (Book Review).	85
Scrubber for Chemical Laboratory Vacuum System.	250	Report of Committee on Fertilizer Legislation, Fertilizer Chemistry Division, Cincinnati Meeting A. C. S.	513
William Lofland Dudley. Obituary.	856	CARPENTER, F. B. Formula for Contents of Cylindrical Tank with Spherical Ends.	517
BATEMAN, E. Method for Zinc Chloride in Treated Wood.	837	CHANDLER, C. F. Herman Frasch. Obituary.	505
BATES, J. S. AND M. C. WHITAKER. Chemical Utilization of Southern Pine Waste.	289	Invention of Celluloid. Note.	601
BECK, G. C. AND S. H. SALISBURY, JR. Study of the Dolomitic Limestones of the Allentown Quadrangle.	753	Presentation Address, Perkin Medal Award.	156
BEDFORD, M. H. AND R. FRANSTEL. New Method for the Determination of Zinc in Treated Wood.	831	CHAPIN, R. M. Blood-Charcoal as a Purifying Agent for Arsenic Solutions Previous to Titration.	1002
BENDER, A. W. Determination of Mercuric Iodide in Tablets.	725	Practical Method for the Preparation of Dry Starch, Soluble in Cold Water, for Use as an Indicator.	649
BENITEZ, J. R., H. J. LUCAS AND R. d'V. SARRAGA. Study of the Milk of Porto Rican Cows.	798	CHURCH, S. R. AND J. M. WATTS. Paraffin Bodies in Coal Tar Creosote and Their Bearing on Specifications.	396
BENSON, H. K. AND J. S. HERRICK. Use of Fine Earth in Mortars.	798	CLARK, C. M. A Convenient Color Camera.	1012
C. A. NEWHALL AND B. TRIMPER. Influence of Organic Admixtures on the Setting of Cement.	798	COLOUREY, H. Note on Electrolytic Determination of Copper.	265
BEROLZHEIMER, D. D. Industry of the Cyanogen Compounds, by H. Koehler. (Book Review).	785	COCHRAN, E. L. AND J. H. PERKINS. Comparative Values of Some Essential Oils as Preservatives of Cane Sugar Solutions.	304
New Publications. . . . .85, 177, 270, 360, 447, 527, 614, 702, 780.	865	Comparative Values of Some Essential Oils as Preservatives of Starch Syrups.	306
BERRYMAN, B. A., C. B. BARDWELL, T. B. BRIGHTON AND K. D. KUHR. Hydrocarbons of Utah. Correction.	865	Effect of High Temperature on Yeast.	480
BIDTEL, E. Note on Valuation of Fluorspar.	263	Influence of Small Amounts of Ethyl Alcohol on Fermentation in Cane Sugar Syrup.	141
BINGHAM, E. C. New Viscosimeter for General Scientific and Technical Purposes.	233	COOLBAUGH, M. F. AND A. ALDER. Volumetric Method for Slightly Elevated Temperatures. A Correction.	398
BISCHOP, H. E. Effect of Bread Wrapping on the Chemical Composition of the Loaf.	736	Cox, H. L. AND C. R. DOWNS. Study of Composition of Water Gas Tar.	366
BLEININGER, A. V. The Silicates in Chemistry and Commerce, by W. Asch and D. Asch. (Book Review).	874	DEL MAR, W. A. Comments of Joint Rubber Insulation Committee on Report of Analytical Committee of Rubber Section A. C. S., April 8, 1914, 515; Note by D. Whipple.	1038
Treatise on Ceramic Industries. Vol. I. Quantitative Inorganic Analysis, by J. W. Mellor. (Book Review).	612		
BOBERT, M. T. Treatise on General and Industrial Organic Chemistry, by Molinari. (Book Review).	768		
BOOTH, L. M. A Comparison Water Softener and Storage Tank.	260		
BOOTH, W. M. Report of Committee on Alum Specifications—Industrial Chemists and Chemical Engineers Division A. C. S.	435		
Correction.	606		
Book Review. Lebensmittelgewerbe, by K. von Buchka. (Book Review).	611		
Natronzellstoff, by Christiansen. (Book Review).	359		
Solvent Oils, Gums, Waxes and Allied Substances, by Hyde. (Book Review).	446		
BOSWORTH, A. W. Use of Sodium Citrate for Determination of Reverted Phosphoric Acid.	227		
BRADY, W. Carbon in Steel by the Direct Combustion Method.	843		
Modern Steel Analysis, by Pickard. (Book Review).	701		
Rapid Methods for the Chemical Analysis of Special Steels, Steel-Making Alloys and Graphite, by C. M. Johnson. (Book Review).	967		

Tentative Specifications and Analytical Procedure for 307 Heater Rubber Insulating Compound. Preliminary Report of the Joint Rubber Insulation Committee, 1911-1914.	75	HALLOCK, A. P. Mineral and Aerated Waters, by C. A. Mitchell. (Book Review).....	84
DERBY, W. B., P. RUDNICK and W. L. LATSWAY. Comparison of Neutral Ammonium Citrate with Sodium Citrate and N/10 Citric Acid.....	486	HAMLIN, M. L. Current Industrial News.....	696
DEWEY, F. P. Determination of Silver and Base Metals in Metal Bullion.....	650, 728	.....259, 348, 428, 507, 594, 690, 778, 859, 953, 1032	
The Pyrometer in the Assay Muffle.....	405	Sammlung von Veweg, Heft 2, Adorgansche, Persulfate und Salzsaure, by F. von Grieswald. Heft 9, Brennerfrage, by D. Sidersky. (Book Review).....	967
DROGS, J. C. Composition of Different Grades of Pack Peas.....	310	HAMMER, B. W. and A. R. JOHNSON. Specific Heat of Milk and Milk Derivatives.....	569
Some Abnormal Factors of So-Called Farmers' Cider Vinegars.....	215	American Institute of Mining Engineers. Pittsburgh Meeting.....	960
DOGE, F. D. Note on Determination of Cmeol.....	863	Cheaper Pig Iron. Note.....	365
DOLLE, R. B. Hypothetical Combinations in Water Analysis.....	710	Editorial: Notices.....	697
DOLLE, R. B. Analytical Analysis of Coal Tar Biscuits.....	206	George Westinghouse. Obituary.....	347
AND A. L. DEAN. Study of Composition of Water Gas Tar.....	366	Industrial Accidents in Pennsylvania in 1912.....	783
DOWDARD, E. Determination of Camphor in Pills and Tablets.....	489	Industrial Poisoning from Fumes, Gases, and Poisons of Manu- facturing Processes, by J. Ramboise. (Book Review).....	526
DUBOIS, G. Chemistry and Properties of Glycero-Phosphates.....	122	Mine Inspectors Institute of U. S. Pittsburgh Meeting.....	606
DUGLEY, W. L. The Chemists' Club. Address.....	419	National Council for Industrial Safety. Chicago Meeting.....	961
DUYSER, C. A. and W. K. LEWIS. New Method for Determining Value of Disinfectants.....	198	Operations of Steel Mills in March. Note.....	356
EASTMAN, E. D. and J. H. HILDEBRAND. Preparation of "Neutral" Ammonium Citrate.....	577	Present Status of the Glass Bottle Industry in the U. S. Note.....	864
EDWARDS, J. D. Determination of Ammonia in Illuminating Gas.....	468	The Commission on Industrial Relations. Editorial.....	274
EDWARDS, V. A. and J. H. HILDEBRAND. Methods for Ex- tractions by Means of Immiscible Solvents from the Point of View of the Distribution Coefficients, II.....	928	The Occupational Diseases, their Causation, Symptoms, Treatment and Prevention, by W. G. Thompson. (Book Review).....	871
ELLIS, C. Analytical Constants of Hydrogenated Oils.....	117	Tin Plate and Steel Mill Operations in Jan., 1914. Note.....	407
ELMS, W. W. and S. HAUGE. Effect of Ferric Salts on Nitrites and the Ortho-Tolidine and Starch-Iodide Tests for Free Chlorine.....	553	HANSON, W. H. Duplex Slide Rule.....	407
EMERY, W. O. Estimation of Acetanilide and Phenacetin in Ad- mixture.....	765	HARDY, J. L. Efficient Method for Cutting Glass.....	238
ENGLE, W. C. and R. P. ANDERSON. Absorption of Gasoline Vapor in Natural Gas by Fuming Sulfuric Acid.....	989	HAUSER, J. J. and J. W. ELMES. Effect of Ferric Salts and Nitrites on the Ortho-Tolidine and Starch-Iodide Tests for Free Chlorine.....	553
EUSTON, E. Constitution of White Lead.....	202	HEARN, W. F. Exhaustive Quantities of Nitrates in Certain Colo- rado Soils.....	586
Nature of Basic Lead Carbonate.....	382	HEBDEEN, J. C. Chemistry of the Bleaching of Cotton Cloth.....	714
EVANS, D. D. and R. P. ANDERSON. Adsorption.....	166	HENDRICK, E. The Colloids Lament. A Poem.....	357
Preliminary Announcement.....	519	HENRI, J. H. and H. K. JENSON. Use of Early Mortars.....	792
EVANS, P. N. The Sentimental Science. Poem.....	519	HERTY, J. H. and C. W. WILLIARD. Effect of Resene on the Lath- ering of Soap Solutions.....	895
FAIRLIE, A. W. Pitot Tubes for Measurement of Gas Velocities.....	583	AND H. L. COX. Stability of Resin Acids at Slightly Elevated Temperatures. Communication.....	882
FALK, K. G. Electrical Conductivity and Ionization Constants of Organic Compounds, by H. Seudder. (Book Review).....	873	AND J. O. GRAYSON. Isoprene from Commercial Turpentine.....	803
Organometallic Compounds of Zinc and Magnesium, by H. Wren. (Book Review).....	873	HESE, B. C. Balance of Trade in Chemical Industries between U. S. and Germany.....	102
Synthetic Use of Metals in Organic Chemistry, by A. J. Hale. (Book Review).....	701	Industry of the Coal Tar Dyes. An Outline Sketch.....	1012
FARAGHER, W. F. Investigation into the Chemistry of Laundering.....	640	Presentation Address. Wm. H. Nichols Medal Award.....	339
FARHAM, G. Report of the Maryland Chemical, Fertilizer Chemistry Division, Cincinnati Meeting A. C. S.....	513	Recommendations of the N. Y. Section of the A. C. S. on the En- largement of the Coal Tar Chemical Industry in the U. S.....	972
FEJELY, M. H., R. E. LEE and J. P. TRICKLEY. Rapid Quanti- tative Analysis of Bronze and Brass (Pb, Cu, Sn, Sb, Fe and Zn).....	556	Relieving the Dyestuff Crisis. Symposium on American Dye Industry.....	953
FISHER, H. L. A Chart of the Carbon Compounds, by C. W. Cuno. (Book Review).....	1047	Some Economic Aspects of Industrial Chemistry, 678; Correction Trade in Chemicals and Chemical Products between Germany and the U. S. in 1913.....	829
FLATHER, J. J. Engineering Thermodynamics, by C. E. Lucke. (Book Review).....	611	AND J. O. GRAYSON. Isoprene from Commercial Turpentine.....	803
FLEMING, R. M. and C. J. HUMPHREY. Toxicity of Various Wood Preservatives.....	128	HILDEBRAND, J. H. and E. D. EASTMAN. Preparation of "Neutral" Ammonium Citrate.....	577
FLITCHER, C. C. Note on Shaker for Mechanical Analysis of Soils. Note, F. Ward.....	517, 1038	HILL, H. W. and W. S. LANDIS. Analysis of Complete Fertilizers Containing Cyanamide.....	20
FORBES, E. B. and C. M. FRITZ. Effects of Ensilage Process on Oxidizability of Forage, R. 224, Note, 605; Note, C. A. Mooers.....	695	HILDEBRAND, W. F. Report of Progress by Industrial Chemists and Chemical Engineers Division Committee on Quality of Platinum Laboratory Utensils, April 9, 1914.....	512
FORSTALL, A. E. Recent Improvements in Gas Manufacture.....	499	HILTON, C. and M. ADAMS. Wood Distillation under Diminished Pressure.....	378
FOX, P. J. Alcohol in the Manufacture of Phosphoric Acid and Phosphates.....	828	HINTZE, C. J. and W. V. CRUESS. Manufacture of Unfermented Grape Juice in California.....	302
Note on the Substitutes for the Blast Lamp.....	940	HIRSCH, A. Electric Furnaces for Heating Steel.....	533
FRANKFORTH, G. B. New Apparatus for Determination of Hydro- gen Sulfide in Water, I.....	676	HOFMANN, R. Travels through the U. S. in Conjunction with the 8th International Congress of Applied Chemistry at New York, by Members of the Congress. Translation.....	49
FRANKLIN, M. W. Air Ozonation.....	850	HOLDE, D. Impressions of 8th International Congress of Applied Chemistry and of Certain Fields of Industry in the U. S. Trans- lation.....	35
Note on Ozone.....	82	HOLLAND, E. B. Determination of Acetyl Number of Oils, Fats, etc.....	482
Use of Ozone in Ventilation. Abstract of Address by L. V. Kupfer FRENCH, E. H. and J. R. WITROW. Present Status of Wood Turpe- ntine Industry.....	959, 148	HOLLEMAN, A. F. Van't Hoff Fund for the Endowment of Research in Pure and Applied Chemistry. Communication to Applicants. HOLMES, A. D. New and Improved Form of Kjeldahl Distillation Apparatus.....	1010
FRITZ, C. W. and E. C. REEBES. Effects of Ensilage Process on Solu- bilities of Flax, 222; Note, 605; Note by C. A. Mooers.....	695	HOSTETTER, J. C. Determination of Magnesium in Calcium Salts.....	392
GAINES, R. H. Coast Erosion and Protection, by Matthews. (Book Review).....	359	HUGHES, F. Sociological Work of the N. J. Zinc Co., 353; Correction HUMPHREY, C. J. and R. M. FLEMING. Toxicity of Various Wood Preservatives.....	128
GAITHER, E. W. and J. W. AMES. Determination of Carbon in Soils and Soil Extracts.....	561	HUSTON, H. A. Remedies for Potash Shortage. Note.....	866
GARDINER, R. F. Note on Utilization of Muds and Scums from Sugar Factories.....	91	HYATT, J. W. Address of Acceptance, Perkin Medal Award.....	158
GARDNER, H. A. Composition of Paint Varnishes.....	104	JACKSON, H. L. Egg Albumin in Baking Powder.....	998
GEER, W. C. Chemistry of Rubber, by B. D. Forth. (Book Review).....	585	JAMIESON, C. S. and R. WRENSHALL. Determination of Triaurin as Phosphate.....	203
GILL, A. H. Manostat for Use in Gas Analysis.....	1047	JAYNE, D. W. Position of the American Tar Distiller. Symposium on American Dye Industry.....	952
GILBERT, H. H. Examination of Lubricating Oils, by T. B. Stillman. (Book Review).....	611	JENKINS, W. M. Method for the Estimation of Specific Heat of Milk and Milk Derivatives.....	560
Exercises in Gas Analysis by Franzen-Callan. (Book Review).....	1037	JONES, C. H. and G. F. ANDERSON. Procedure for Separating Or- ganic Ammoniates from the Mineral Portion of Commercial Fertilizers.....	580
GOMBERG, M. The Existence of Free Radicals. Abstract of Address of Acceptance, Wm. H. Nichols Medal Award.....	339	KALMUS, H. T. Oxides of Cobalt.....	115
GRABER, H. T. Laboratory Studies on Malt Extract.....	403	Preparation of Metallic Cobalt by Reduction of the Oxide.....	107
GRAHAM, J. O. and C. H. HERTY. Isoprene from Commercial Turpe- ntines.....	803	KATAYAMA, T. Study of Crude Petroleum from Bioritsu, Formosa.....	469
GRAV, C. P. Workings of the California Insecticide Law.....	590	KEAY, J. A. Estimation of Sulfite by Digestion and Evaporation in Mills at Grand' Mere, Quebec.....	26
GRAV, T. Untersuchung der Kohlenwasserstoffoel und Fette, by KERN, R. F. Details of Cyanide Practice, by H. A. Megraw. (Book Review).....	612	KEPNER, B. H. Physical Factors which Influence the Percentage of Wet and Dry Gluten in Wheat Flour.....	481
GRAFFIN, M. L. Chemical Evaluation of Wood for Pulp.....	360	KERN, R. F. Details of Cyanide Practice, by H. A. Megraw. (Book Review).....	613
Evaluation of Pulpwood. Note.....	163	The Nickel Industry: With Special Reference to the Sudbury Region, Ontario, by A. P. Coleman. (Book Review).....	527
GROSH, D. M. Chemical Industries and Schools.....	244	KERR, R. H. Note on Detection of Nickel in Fat.....	207
Treaty of Gila River Natural Aluminum Sulfate in Water Purifi- cation.....	608	KIRKALL, D. Mechanical Problems of Ventilation. Address at Ventilation Symposium.....	348
GUEDMAN, E. Standards of Food and Drug Chemists.....	687	KIRSCHBAUM, L. Cementing Value of Bituminous Binders.....	976
HABER, F. Modern Industrial Chemistry. Hurter Memorial Lecture HABER, F. E. Route for the Blast Lamp.....	325	KNIGHT, G. W. Determination of Prussian Blue in Tea.....	909
Chemical Filtration.....	632	KOBER, P. L. Importance of Enzymes and En- zyme Reactions in Medicine and Surgery.....	855





Neutral Ammonium Citrate with Sodium Citrate and N/10 Citric Acid.....	486	A Comparison of the Reduction of the Different Members of the B. Coli Group.....	637
SAKURAI, J. On Dr. Backeland's Visit to Japan. Note.....	866	THOMAS, S. J. Hypochlorite of Lime Treatment of a Municipal Water Supply and Study of Certain Resistant Bacteria.....	548
SALT, F. D. AND J. B. THOMAS. Thermochemical Method for the Determination of the Purity of Platinum Ware.....	452	THOMPSON, G. W. Chairman's Address, Perkin Medal Award.....	153
SALISBURY, S. H., JR., AND G. C. BECK. Study of the Dolomitic Limestones of the Mountaintop Quadrangle.....	847	Chemistry as Affecting the Profitableness of Industry.....	152
SARASIN, E. AND J. B. THOMAS. Some Further Results of the Hypochlorite Disinfection of the Baltimore City Water Supplies.—A Comparison of the Reduction of the Different Members of the B. Coli Group.....	637	Remarks on White Lead Paint Published in 1810.....	266
SARGENT, W. Modified Electrical Insulation and Plastics, by Hemmings. (Book Review).....	146	HOMPSON, W. H. Ozone.....	170
SÁRRAGA, R. D'V., H. J. LUCAS AND J. R. BENITEZ. Study of the Milk of Porto Rican Cows.....	22	TOCHI, M. Chemistry of Pine Oil.....	720
SCALLONE, C. C. AND C. E. BURKE. Investigations on Oil of Black Sage.....	804	Torrent Patent Situation. Address.....	677
SCHAEFER, H. H. AND H. V. ARNY. Ferric Alum Estimation of Caseine.....	748	TOROSSIAN, G. Iodine Recovered from Waste Liquor in Copper Titrations. Note.....	83
SCHAEFFER, J. A. Lead Contents in Sublimed White Lead—A Calculation.....	300	TREMPER, B., H. K. BENSON AND C. A. NEWELL. Influence of Organic Ammixtures on the Setting of Cement.....	795
SCHOCH, E. P. Toxicity of Various Wood Preservatives. Note.....	603	TRICKERY, J. F. AND E. L. JONES. Analysis of Bronze and Brass (Pb, Cu, Sn, Sb, Bi, and Zn).....	556
SCHOLL, C. AND E. BARTOW. Comparative Value of Calcium and Magnesium-Calcium Lime for Water Softening.....	189	TROWBRIDGE, P. F. AND C. R. MOULTON. Estimation of the Lime Requirement of Soils by Means of the Hydroxides of the Alkaline Earths.....	835
Oil Port Oils, Cedar Wood, and Gum Observations on $\alpha$ -Pine Oils of the Coniferae. I.—The Leaf and Twig Oils of Cuban and Longleaf Pines and the Cone Oil of Longleaf Pine.....	631	TUCKER, S. A. Electric Furnace, Its Construction, Operation and Uses, by A. Stansfield. (Book Review).....	525
II.—The Leaf and Twig, and Bark Oils of White Fir.....	723	Laboratory Course in Electrochemistry, by O. P. Watts. (Book Review).....	1047
III.—The Leaf and Twig and the Cone Oils of Western Yellow Pine and Sugar Pine.....	809	TUTTLE, J. B. AND W. H. SMITH. Iodine Number of Linseed and Petroleum Oils.....	994
Study of Authentic Samples of Gum Turpentine.....	893	Printing Inks and Their Analysis.....	659
SCHOTT, S. M. AND E. E. WARE. Paint Films as Protective Coatings for Concrete.....	184	TWITCHELL, E. Melting and Solidifying Points of Mixtures of Fatty Acids and the Use of These Points to Determine the Composition of Such Mixtures.....	564
SCHUEPPHARD, J. Determination of Cellulose. Note.....	440	ULRICH, W. H. AND J. C. OLSEN. Ozone in Ventilation.....	619
SCHUMANN, C. L. AND E. E. WARE. Examination of Chinese Wood Oil.....	806	UTT, A. A. Some Characteristics of Chlorine-Bleached Flour.....	728
SCOTT, J. M. AND J. F. SNELL. Analysis of Maple Products. III. Range of Variation of Analytical Values in Genuine Maple Syrup.....	216	Some Data on Peanut Butter.....	746
SEIBERT, F. M. AND G. A. BURRELL. Experiments with Small Animals and Carbon Monoxide.....	241	VANDERPOEL, F. Personal Reminiscences, Perkin Medal Award.....	161
SEIDELL, A. Improvements in the Iodine Pentoxide Method for Carbon Monoxide in Air.....	298	VOSMAER, A. Applications of Ozone.....	229
AND P. W. MESERVE. Determination of Minute Amounts of Sulfur Dioxide in Air.....	321	WAGGAMAN, W. H. Reserve Supply of Phosphate Rock in the U. S.....	464
SHARPLES, P. P. Relation between Melting Point and Viscosity of Refined Tars.....	285	WAGNER, T. B. Effect of Legislation upon Chemical Industries. Presidential Address at 6th Annual Meeting of American Institute of Chemical Engineers.....	71
SHERMAN, H. C. Chemical Technology and Analysis of Oils, Fats and Waxes, Vol. I, by Lewkowitch.....	660	WALKER, P. H. AND L. H. BAILEY. Simple Extraction Apparatus.....	356
SHY, R. C. Investigation of the Dusts of Alfalfa and the Effect of Rapid Curving upon the Food Value of Alfalfa.....	176	WALKER, W. O. Rapid Method for Casein in Milk, 131, Correction, and A. F. C. ALLEN. Note on Food Analysis.....	573
SMITH, A. Chemistry in America, by E. F. Smith. (Book Review).....	910	WARD, F. Shaker for Mechanical Analysis of Soil, 147, Note.....	1038
SMITH, W. H. AND J. B. TUTTLE. Iodine Number of Linseed and Petroleum Oils.....	966	WARE, E. E. AND C. L. SCHUMANN. Examination of Chinese Wood Oil.....	806
Printing Inks and Their Analysis.....	659	AND S. W. SCHOTT. Paint Films as Protective Coatings for Concrete.....	184
SNELL, J. F. AND A. G. LOCHHEAD. Composition of Maple Syrup Sand.....	301	WEISS, J. M. Coal Tar Distillation, by A. R. Warnes. (Book Review).....	612
AND M. M. SCOTT. Range of Variation of Analytical Values in Genuine Maple Syrups.....	216	"Free Carbon" in Tar Products.....	279
SOMERMEIER, E. E. Lower Limits of Combustible Mixtures of Gas and Air.....	191	AND S. R. CHURCH. Paraffin Bodies in Coal Tar Cresote and Their Bearing on Specifications.....	396
Partial and Intermittent Combustion of Gas.....	374	WEITH, A. J., L. V. REDMAN AND F. P. BROCK. Determination of Phenol in Presence of Hexamethylenetetramine and Formaldehyde.....	263
SOPER, G. A. Review of the Examination of Water and Water Supplies, by Thresh. (Book Review).....	176	WELLS, C. A. Cottonseed Flour as a Possible Food for Man.....	338
STEINKOENIG, L. A. Distribution of Certain Constituents in the Separates of Loam Soils.....	576	WENDELL, G. V. Practical Science for Engineering Students, by Stanley. (Book Review).....	446
STIEGLITZ, J. Annual Tables of Constants. III. Note.....	171	WESSON, L. G. Combustion Method for Direct Determination of Rubber.....	459
STILLWELL, A. G. Note on Influence of Rate of Stirring on Titre Determinations in Fats.....	517	WHIPPLE, D. W. Report of Analytical Committee, Rubber Section, Cincinnati Meeting, A. C. S., 514, Note.....	1038
St. John, A. D. Proposed New Standard Loop for Use in Bacteriological Tests of Disinfectants.....	604	WHITAKER, M. C. Accident Prevention, by J. R. Douglas (Book Rev.).....	85
STONE, G. C. General Metallurgy by Hofman. (Book Review).....	940	Dictionary of Applied Chemistry. Vols. IV and V, by Thorpe. (Book Review).....	173
Metallurgy of Copper, by H. O. Hofman. (Book Review).....	1045	Some Professional Obligations. Presidential Address, Troy Meeting, American Institute of Chemical Engineers.....	599
STONE, I. F. Coal in Colors of America. Symposium on American Dye Industry.....	946	Process Co. (Book Review).....	701
STRATTON, S. W. Bureau of Standards' Analyzed Samples.....	171	AND J. S. BATES. Chemical Utilization of Southern Pine Waste.....	289
STRONG, W. W. Instantaneous Thermostat and Smoke and Fume Monitors, Precipitators and Recorders.....	848	AND W. F. RITTMAN. Thermal Reactions in Carbureting Water Gas. I.—Theoretical, 383; II.—Experimental.....	472
SULLIVAN, E. C. AND W. C. TAYLOR. Some Rapid Methods for Glass Analysis.....	897	WHITTEMORE, C. F. AND R. B. MOORE. Radioactivity of the Waters of Saratoga Springs, N. Y.....	552
SULLIVAN, M. X. Nitrates in Colorado Soils. Editorial.....	532	WIGLE, A. E. AND I. W. BATES.....	83
Origin of Vanillin in Soils—Vanillin in Wheat and in the Water in Which Wheat Seedlings Have Grown.....	919	WILLIAMETTE PULP AND PAPER CO. Note on Platinum Thief.....	83
SWEETLAND, E. J. Filter Presses.....	142	WILLIAMS, W. AND H. HARRIS. Low Temperature Solu- tions of Soap Solutions.....	1038
TAKAMINE, J. Enzymes of Aspergillus Oryzae and the Application of its Analyses to the Determination of Industrial Inclusions.....	824	WILKIN, I. G. AND W. H. MANN. Carbonates as Sources of Lime.....	253
TARBELL, R. F. Determination of Arsenic in Hydrochloric and Sulfuric Acids.....	400	WINSLOW, C. E. AND A. N. Y. State Commission on Ventilation and Its Problems. Address at Ventilation Symposium.....	1045
TARTAR, H. V. Theoretical Basis for Proportions of Lime and Sulfur in Commercial Preparation of Lime-Sulfur Spray.....	313	Withrow, J. R. Industrial Chemistry for Engineering Students, by H. K. Benson. (Book Review).....	173
Valuation of Lime-Sulfur as an Insecticide.....	95	Transactions, American Institute of Chemical Engineers. Vol. V. (Book Review).....	148
TASSIN, W. Metallography as Applied to Inspection.....	845	AND E. H. FRENCH. Present Status of Wood Turpentine Industry.....	203
TAYLOR, G. B. Apparatus for the Analysis of Complex Gas Mixtures.....	788	WRENSHALL, R. AND G. S. JAMIESON. Determination of Titanium as Phosphate.....	822
TAYLOR, W. C. AND E. C. SULLIVAN. Some Rapid Methods for Glass Analysis.....	897	WRIGHT, P. A. AND L. S. PALMER. Ethyl Ester of Linolic Tetra bromide as a Product in the Analysis of Cottonseed Oil.....	822
THOMAS, A. W. Industrial Organic Analysis, by P. S. Arup. (Book Review).....	788	YOUNGMAN, R. H. Effect of Steam upon Magnesite Brick or Calcined Magnesite.....	
THOMAS, J. B. AND E. A. SANDMAN. Some Further Results of the Hypochlorite Disinfection of the Baltimore City Water Supplies—			

# SUBJECT INDEX

## THE JOURNAL OF INDUSTRIAL AND ENGINEERING CHEMISTRY VOLUME VI, 1914

<b>ABRASIVE MATERIALS</b> , Production of. F. I. Katz. Gov. Pub.	784	<b>Antipyrim</b> , Estimation of. W. O. Emery and S. Palkin.	751
<b>Absorption of Water</b> by Building Brick. H. W. Mahr.	809	<b>Antiseptics</b> , Note on. H. T. Brooks.	958
<b>Abstracting</b> , Chemical. J. J. Miller.	411	<b>Arsenic Acid</b> , Reduction to Arsenious Acid by Thioisulfuric Acid.	608
<b>Accidents, Industrial, in America, in 1913.</b> Note.	261	R. M. Chapin. Gov. Pub.	608
<b>Accidents, Industrial, in Mass.</b> Note.	509	<b>Arsenic in Hydrochloric and Sulfuric Acids</b> , Determination of. R. F.	400
<b>Accidents, Industrial, in Pa. in 1912.</b> W. A. Hamor.	81	<b>Arsenic Solutions</b> , Blood-Charcoal as a Purifying Agent for, Previous	1002
<b>Accumulator Electrolytes</b> , Note.	862	to Titration. R. M. Chapin.	1002
<b>Acetanilide and Phenacetin in Admixture</b> , Determination of. W. O.	665	<b>Arsenical Cattle Dips</b> : Methods of Preparation and Directions for	963
Emery.	665	Use. R. M. Chapin. Gov. Pub.	963
<b>Acetyl Number</b> , Determination of. E. B. Holland.	1013	<b>Arsenical Dipping Fluids</b> , Laboratory and Field Assay of. R. M.	520
<b>ADAMSSES</b> . C. 148, 399, 425, 407, 499, 586, 677, 765, 850, 941.	831	Chapin. Gov. Pub.	1042
<b>Adsorption</b> , Selective. E. G. Parker.	521	<b>Asbestos</b> , S. S. Diller. Gov. Pub.	133
<b>Aerology</b> , Standard Units in. Gov. Pub.	445	<b>Asphalts</b> , Penetration, New Electrically Controlled and Timed,	286
<b>Agricultural (Nutrition) Paper</b> . Gov. Pub.	248	and Effect on Penetrations of Variations in Standard Needles. H. W.	606
<b>Agricultural Research, Journal of</b> . Gov. Pub.	625	Mahr.	976
<b>Apparatus for Taking Dust and Bacteria Samples of</b> . C. Baskerville.	828	<b>Asphalts</b> , Differentiation of Natural and Oil. E. C. Pailler.	405
<b>Alcohol, Ethyl</b> , Influence of Small Amounts of, on Fermentation in	548	<b>Asphalts</b> , Cementing Value of Bituminous Binders. L. Kirschbraun	608
Cane Sugar Syrup. C. B. Cochran and J. H. Perkins.	548	Assay Muffle, The Pyrometer in the. F. P. Dewey.	608
<b>Alcohol, Ethyl</b> , Manufacture of, from Wood Waste. Preliminary	548	<b>Atmospheric Transparency for Radiation</b> . F. E. Towle. Gov. Pub.	608
Experiments on the Hydrolysis of White Spruce. F. W. Kressman.	548		
<b>Alcohol in the Manufacture of Phosphoric Acid and Phosphates</b> .	548		
P. J. Fox.	548		
<b>Alcohol</b> , Production and Use of Denatured, in Principal Countries.	548		
C. A. Crampton. Gov. Pub.	548		
<b>Alcohol</b> , Reports on, Decisions. Gov. Pub.	548		
<b>Alfalfa</b> , An Investigation of the Diastase of, and the Effect of Rapid	548		
Curing upon the Food Value of Alfalfa. R. C. Shuey.	548		
<b>Alloys</b> : A New Bearing Metal. Note.	548		
<b>Alloys</b> , Commercial, Report of Committee to Division of Industrial	548		
Bureau of Mines Report. Abstract.	548		
<b>Alloys</b> , Copper, Tin and Silicon, Analysis of. Note. E. D. Koeppling.	548		
<b>Alum in Foods</b> . Gov. Pub.	548		
<b>Alum</b> , Specific Name, Report of Committee to Division of Industrial	548		
Chemists and Chemical Engineers at Cincinnati Meeting of A. C. S.	548		
W. M. Booth, 435; Correction and Note.	548		
<b>Aluminum Alloys</b> : The Altiar Process of Die-Casting. Note.	548		
<b>Aluminum Compounds</b> , Soluble, Their Occurrence in Certain Vegetable	548		
Products. C. C. Myers and C. Voegtlin. Gov. Pub.	548		
<b>Aluminum Sulfate and Color in Mechanical Filtration</b> , The Relation	548		
between. F. E. Hale.	548		
<b>Aluminum Sulfate</b> , Test of Gila River Natural, in Water Purifica-	548		
tion. D. M. Grosh.	548		
<b>AMERICAN CHEMICAL SOCIETY</b>	548		
49th (Spring) Meeting, Cincinnati, April 6 to 10, 1914.	548		
Announcement, 171; Program, 171; Excursions.	548		
Editorial, 364; Program of Papers, 431; Excursions.	548		
Fertilizer Chemistry Division Report.	548		
Alum Specifications Committee Report.	548		
Fertilizer Legislation Committee Report.	548		
Phosphoric Acid Committee Report.	548		
Report of Analytical Committee of Rubber Section, 514; Note.	548		
Note by Del Mar.	548		
Report of Progress by Committee on Quality of Platinum Labo-	548		
ratory Utensils.	548		
50th (Annual) Meeting, Montreal, September, 1914.	548		
Date of Meeting Changed.	548		
Meeting Postponed Indefinitely. Editorial.	548		
Meeting Called off.	548		
Note on 1914 Directory.	548		
Recommendations of the N. Y. Section on the Enlargement of the	548		
Coal-Tar Chemical Industry in the U. S. B. C. Hesse.	548		
<b>American Electrochemical Society</b>	548		
25th General Meeting, New York, April 16 to 18, 1914.	548		
Program of Papers.	548		
Presidential Address. E. F. Roeber. Report of Pittsburgh Meet-	548		
ing, October 8 to 10, 1914. W. A. Hamor.	548		
<b>American Gas Institute</b> . 9th Annual Meeting, October 21 to 23, 1914.	548		
Program.	548		
<b>American Institute of Chemical Engineers</b> . 29th Meeting, Pitts-	548		
burgh, April 9 to 11, 1914. Report of Meeting.	548		
<b>American Institute of Engineers</b> . Report of Pittsburgh Meet-	548		
ing, October 8 to 10, 1914. W. A. Hamor.	548		
<b>American Leather Chemists' Association</b> . Program Chicago Meet-	548		
ing, October 28 to 31, 1914.	548		
<b>Ammonia in Illuminating Gas</b> , Determination of. J. D. Edwards.	548		
<b>Ammoniates</b> , Organic, A Procedure for Separation of, from the Mineral	548		
Acids of Conts of Fertilizers. C. H. Jones and C. F. Anderson.	548		
<b>Ammonium Chloride</b> , a New By-Product of Gas Works, etc. Note.	548		
<b>Ammonium Chloride</b> , "Neutral," The Preparation of. E. D. Eastman	548		
and J. H. Hildebrand.	548		
<b>Ammonium Citrate</b> , An Exact and Easy Method for Pre-	548		
paring a Neutral. J. M. McCandless.	548		
<b>Ammonium Citrate Solution</b> , Neutral, Compared with Sodium	548		
Citrate and N/10 Citric Acid. P. Rudnick, W. B. Derby and	548		
W. Latsch.	548		
<b>Ammonium Sulfate and Sodium Nitrate in 1913</b> . Note.	548		
<b>Ammonium Sulfate</b> , German and English Exports in 1912 and 1913	548		
Note.	548		
<b>Antipyrim</b> , Estimation of. W. O. Emery and S. Palkin.	751		
<b>Antiseptics</b> , Note on. H. T. Brooks.	958		
<b>Arsenic Acid</b> , Reduction to Arsenious Acid by Thioisulfuric Acid.	608		
R. M. Chapin. Gov. Pub.	608		
<b>Arsenic in Hydrochloric and Sulfuric Acids</b> , Determination of. R. F.	400		
<b>Arsenic Solutions</b> , Blood-Charcoal as a Purifying Agent for, Previous	1002		
to Titration. R. M. Chapin.	1002		
<b>Arsenical Cattle Dips</b> : Methods of Preparation and Directions for	963		
Use. R. M. Chapin. Gov. Pub.	963		
<b>Arsenical Dipping Fluids</b> , Laboratory and Field Assay of. R. M.	520		
<b>Asbestos</b> , S. S. Diller. Gov. Pub.	1042		
<b>Asphalts</b> , Penetration, New Electrically Controlled and Timed,	133		
and Effect on Penetrations of Variations in Standard Needles. H. W.	286		
<b>Asphalts</b> , Differentiation of Natural and Oil. E. C. Pailler.	606		
<b>Asphalts</b> , Cementing Value of Bituminous Binders. L. Kirschbraun	976		
<b>Assay Muffle</b> , The Pyrometer in the. F. P. Dewey.	405		
<b>Atmospheric Transparency for Radiation</b> . F. E. Towle. Gov. Pub.	608		
<b>BACTERIA</b> , A Study of Certain Resistant, and the Hypochlorite of	548		
Lime Treatment of a Municipal Water Supply. S. J. Thomas.	866		
<b>Baekeland</b> , Dr. Leo H., in Japan. Note. J. Sakurai.	998		
<b>Baking Powder</b> , Egg Albumin in. H. L. Jackson.	1032		
<b>Balance of Trade in Chemical Industries between U. S. and Germany</b> .	965		
<b>Barite Deposit</b> near Wrangell, Alaska. E. F. Burchard. Gov. Pub.	444		
<b>Barometers</b> , Testing of. Gov. Pub.	786		
<b>Barometric Reading</b> , Conversion of, into Standard Units of Pressure.	1042		
<b>Barytes</b> , J. M. Hill. Gov. Pub.	25		
<b>Belladonna</b> , Study of American Growth. F. A. Miller and R. N. Reed.	445		
<b>Benzene Derivatives in Soils</b> , Presence of Some. E. C. Shorey. Gov.	518		
<b>Benzoic Acid</b> in Prunes and Cranberries. Note on Quantity of. M. J.	430		
Radin.	259		
<b>Benzol and Tar Prices</b> , 1880-1903. Note.	963		
<b>Benzoic Acid</b> in Prunes and Cranberries. Note on Quantity of. M. J.	976		
<b>Biological Products</b> Establishments, Licensed Propagation and Sale	940		
of Viruses, Serums, Toxins and Analogous Products. Gov. Pub.	714		
<b>Bituminous Binders</b> , The Cementing Value of. L. Kirschbraun.	259		
<b>Blanching of Cotton Cloth</b> , Chemistry of the. J. C. Hadden.	786		
<b>Boiler Explosions in Chemical Industries in Germany in 1912</b> . Note.	922		
<b>Boiler Furnaces</b> , Factors Governing Combustion of Coal in. J. K.	1038		
Brem, J. C. Frazer and V. E. Augustine. Gov. Pub.	515		
<b>Bone Meal</b> , Influence of Fineness upon the Availability of. S. S.	512		
Peck.	556		
<b>BOOK REVIEWS</b> (see separate heading below).	785		
<b>Brass and Bronze</b> , Method for the Rapid Quantitative Analysis of	736		
(Pb, Cu, Sn, Zn, Sb, Fe and Zn). R. E. Lee, J. P. Trickey and W. H.	1037		
Fegely.	953		
<b>Brass-Furnace Practice in the U. S.</b> H. W. Gillett. Gov. Pub.	1042		
<b>Bread</b> , Effect of Wrapping on the Chemical Composition of the Loaf.	556		
H. E. Barnard and H. E. Bishop.	650		
<b>Brick Building</b> , Studies on the Absorption of Water by. H. W. Mahr.	165		
<b>Brick</b> , Building, Studies on the Absorption of Water by. H. W. Mahr.	406		
<b>Brick</b> , Magnesian, or Calcined Magnesian, The Effect of Steam on.	518		
<b>British Association for the Advancement of Science</b> , President's Ad-	941		
dress before the Chemical Section of. Abstract. W. J. Pope.	136		
<b>Bromine</b> , Salt and Calcium Chloride, The Production of, in 1913.	85		
<b>Bronze and Brass</b> , Method for the Rapid Quantitative Analysis of	525		
(Pb, Cu, Sn, Sb, Fe and Zn). R. E. Lee, J. P. Trickey and W. H.	85		
Fegely.	173		
<b>Bullion</b> , Precious Metal Determination of Silver and Base Metal in.	1046		
F. P. Dewey.	171		
<b>Bureau of Mines Budget</b> to June 30, 1915.	446		
<b>Bureau of Mines Experiment Station at Pittsburgh</b> , Approved.	1046		
<b>Bureau of Standards' Analyzed Samples</b> . S. W. Stratton. Sheet	446		
Brem, J. C. Frazer and V. E. Augustine. Gov. Pub.	873		
<b>Burette</b> , A Convenient Form of Weighing. H. S. Bailey.	966		
<b>Butterfat</b> , Apparatus and Method for Hardness. A. E. Perkins.	612		
<b>BOOK REVIEWS</b> . 84, 173, 268, 358, 446, 524, 611, 701, 787, 871, 966,	85		
<b>Accident Prevention</b> , by Douglas, M. C. Whitaker.	525		
<b>Agricultural Analysis</b> , Principles and Practice of, by Wiley. F. K.	85		
<b>Agricultural Chemistry</b> , Principles of, by Fraps. F. B. Carpenter.	173		
<b>American Institute of Chemical Engineers</b> , Transactions. Vol. V.	1046		
<b>Ammonia</b> Institute of Chemical Engineers, Transactions. Vol. V.	171		
<b>Annual Tables of Constants</b> , etc. Vol. III. Note.	446		
<b>Asphalts</b> , Chemistry and Technology of Natural and Artificial (Ger-	1046		
man). by Kohler. C. Richardson.	873		
<b>Carbon Compounds</b> , Chart of the, by Cuno. H. L. Fisher.	966		
<b>Cattle Feeding and Dairying</b> , The Chemistry of, by Murray. C. A.	612		
<b>Cement</b> , National Standard, by Christensen. S. Born.	789		
<b>Ceramic Industries</b> , Treatise on. Vol. I. Quantitative. Inorganic	359		
Analysis, by Mellor. A. V. Bleining.	612		
<b>Charcoal and Lampblack</b> , Manufacture of, by Kohler.	1046		
<b>Chemistry and its Borderland</b> , by Stewart. F. Barry.	873		
<b>Chemistry in America</b> , by Smith. A. Smith.	966		
<b>Coal Tar Distillation</b> , by Warnes. J. M. Weiss.	612		



Coal-Tar Industry, by Lunge and Kohler, Vol. I. Neues Handbuch der Chemischen Technologie. R. K. Murphy.	1046
Coast Erosion and Protection, by Matthews. R. H. Gaines.	359
Constants, Electrical Conductivity and Ionization, of Organic Compounds, by Seudler, R. K. Falk.	873
Copper, Metallurgy, of, by Hofman. G. C. Stone.	1045
Cyanide Practice, Details of, by Megraw. E. F. Kern.	613
Cyanogen Compounds, The Industry of the (German), by Koehler. D. B. Zerolzheimer.	788
Dairying and Cattle Feeding, The Chemistry of, by Murray. C. A. Browne.	589
Dextrose: Der Starkekerzer, by Wichelhaus. C. A. Browne.	558
Dictionary of Applied Chemistry. Vols. IV and V, by Thorpe. M. C. Whitaker.	173
Diseases, Occupational, Their Causation, Symptoms, Treatment and Prevention, by Thompson. W. A. Hamor.	871
Distillery Practice (German), by Sidersky. M. L. Hamlin.	967
Dyeing, Chemistry of, by Wood. J. M. Matthews.	873
Electric Furnace, The. Its Construction, Operation and Uses, by Stanfield. S. A. Tucker.	638
Electrochemistry, Laboratory Course in, by Watts. S. A. Tucker.	1047
Engineering Students, Practical Science for, by Stanley. G. V. Wendell.	417
Engineering Thermodynamics, by Fickler. J. F. Flather.	611
Fuel and Gas Analysis, Technical, by White. E. G. Bailey.	81
Gas Analysis, Exercises in, by Franzen. A. H. Gill.	941
Gas and Fuel Analysis, Technical, by White. E. G. Bailey.	81
Industrial Chemistry for Engineering Students, by Benson. J. R. Withrow.	1045
Insulation, Molded Electric, and Plastics, by Hemming. W. Sanger.	146
Lebensmittelgewerbe, Das, by von Buchka. S. Born.	611
Metallography, by Desch. W. Campbell.	858
Metallurgical Analysis, by Lord-Demoire. W. Brady.	175
Metallurgy, General, by Hofman. G. C. Stone.	174
Metals, The Synthetic Use of, in Organic Chemistry, by Hale. K. G. Falk.	701
Metals, Welding and Cutting of; Oxyacetylene Process. M. C. Whitaker.	701
Nickel Industry, The. With Special Reference to the Sudbury Region, Ontario, by Coleman of Canadian Mines Department. E. F. Kern.	872
Nitrogen, Fixation of Atmospheric, by Knox. A. Lowy.	1046
Oils, Examination of Lubricating, by Stillman. A. H. Gill.	1047
Oils, and Waxes, Chemical Technology and Analysis of, by Lewkowitch. Vol. I. H. C. Sherman.	176
Oils, Hydrocarbon, Analysis of (German), by Holde. T. T. Gray.	613
Oils, Solvent, Gums, Waxes and Allied Substances, by Hyde. S. A. Tucker.	416
Organic Analysis, Allen's Commercial. Vol. III, by Davis and Sadtler. J. H. Long.	874
Organic Analysis, Industrial, by Arup. A. W. Thomas.	888
Organic Chemistry, The Synthetic Use of Metals in, by Hale. K. G. Falk.	701
Organic Chemistry, Treatise on General and Industrial, by Molinari. M. T. Bogert.	768
Organometallic Compounds of Zinc and Magnesium, by Wren. E. G. Bailey.	873
Peroxides and Persalts, Inorganic (German), by von Giesebrand. M. L. Hamlin.	967
Petroleum Industry, Scientific Aspects of the (German), by Gurwitsch. R. K. Murphy.	85
Plastics and Molded Electrics, by Hemming. W. Sanger.	146
Poisoning, Industrial, from Fumes, Gases and Poisons of Manufacturing Processes, by Rambousek. W. A. Hamor.	876
Preservative Coatings for Structural Materials, by Am. Soc. Testing Materials.	269
Rare Earths, Analysis of (German), by Böhm. J. M. Lenher.	81
Resins, Chemical, and Rubber-Chemical, by J. M. Lenher.	81
Rubber, Chemistry of, by Porritt. W. C. Geer.	1047
Silicates in Chemistry and Commerce, The, by Asch and Asch. A. V. Bleiminger.	873
Steel Analysis, Modern, by Pickard. W. Brady.	874
Steels, Special, Steel-Making Alloys and Graphite, Rapid Methods for the Chemical Analysis of, by Johnson. W. Brady.	967
Sugar Analysis, by Wiechmann. C. A. Browne.	576
Sugar Manufacture, Plantation White, by Harloff. C. A. Browne.	175
Sugars and Their Simple Derivatives, by Mackenzie. J. M. Nelson.	701
Tannins, Monograph, by Dekker-Klipp. O. Kress.	609
Tar, Coal, Distillation, by A. R. Warner. J. M. Weiss.	612
Taschenbuch für die anorganisch-chemische Grossindustrie, by Lunge and Berl. R. K. Murphy.	613
Thermodynamics for Chemists, by G. N. Lewis. O. Kress.	613
Thermodynamics, Textbook of, by Partington. H. L. Parr.	58
Water and Water Supplies, Review of Examination of, by Thresh. G. A. Super.	176
Waters, Mineral and Aerated, by Mitchell. A. P. Hallock.	81
Waters, underground, for Commercial Purposes, by Rector. A. M. Bowell.	701
Welding and Cutting of Metals, Oxyacetylene Process, by Vulcan Process Co. M. C. Whitaker.	701
<b>CALCIUM</b> Carbide, Cyanamide and Nitrate. World's Output in 1913. Note.	81
Calcium Chloride, Salt and Bromine, Production of, in 1913. W. C. Hostetter.	967
Calcium Salts, Method for Determination of Magnesium in. J. C. Hostetter.	967
Calorimeter, Coal, A New. Note.	807
Calorimeter, Respiration, and Results of Experiments with It. C. F. Langworthy and R. D. Milner. Gov. Pub.	445
Calorimetric Resistance Thermometers, New. H. C. Dickinson and E. F. Mueller. Gov. Pub.	445
Calorimetry, Industrial Gas. C. W. Waldner and E. F. Mueller. Gov. Pub.	445
Camphor and Certain Essential Oils, Rapid Method for Determination of, when in Solution in Alcohol. W. B. D. Penniman and W. W. Randall.	926
Camphor in Tablets and Pills, Determination of. E. Doward.	489
Carbon, Determination of, in Soils and Soil Extracts. J. W. Ames and E. W. Gaither.	501
Carbon, "Free," in Tar Products. J. M. Weiss.	276
Carbon in Steel and Iron, by the Barium Carbonate Titration Method. J. R. Cain. 465; Gov. Pub.	609
Carbon in Steel by the Direct Combustion Method. W. Brady.	843
Carbon Monoxide, Experiments with Small Animals. G. A. Burrell and F. M. Seibert.	241
Carbon Monoxide in Air, Improvements in Iodine Pentoxide Method for Determination of. A. Seidel.	321
Carotolite near Mauch Chunk, Pa. E. T. Wherry. Gov. Pub.	964
Casene, Ester and Isolation of, by H. V. Arny and H. H. Schaefer.	359
Casene in Milk, Rapid Method for. W. O. Walker. 131; Correction.	356
Celestite Deposits in Cal. and Ore. W. C. Phalen. Gov. Pub.	785
Celite, Synthetic, and Large Crystals of Tricalcic Silicate. E. D. Campbell.	701
Cellulose, The Invention of. Editorial. L. H. Baekeland. 90; Note.	606
R. C. Schupphaus, 440; Note. C. F. Chandler.	701
Cement, Influence of Organic Admixtures on the Setting of. H. K. Benson. C. A. Newhall and B. Tremper.	795
Cement Plants, Determination of Dust Fall in the Neighborhood of. J. P. Mitchell.	454
Cement, Portland, U. S. Specification for. Gov. Pub.	698
Cement, Production of Portland, in 1913. U. S. Geol. Survey Note.	166
Cement: Syntactic Colite and Large Crystals of Tricalcic Silicate. E. D. Campbell.	706
Census, Report of 13th: Vol. X—Manufactures; Vol. XI—Mines and Quarries. Gov. Pub.	443
Chemical Statistics, by Evans. Gov. Pub.	869
Centennial Exposition at Dusseldorf. Note.	350
Ceramics: Cost of Production in Pottery Industry. Gov. Pub.	963
Ceramics: Statistics of the Pottery Industry, 1913. J. Middleton. Gov. Pub.	1043
Ceramics: Studies on the Absorption of Water by Building Brick. H. W. Mahr.	800
Ceramics: Veritas Firing Rings. A. V. Bleiminger and G. H. Brown. Gov. Pub.	870
Chandler, Foundation Lecture—1914. Some Aspects of Industrial Chemistry. L. H. Baekeland.	769
Cheese Fat, Composition of Roquefort. J. N. Currie. Gov. Pub.	963
Cheese of Cheddar Type, Bacteria Concerned in Production of Characteristic Flavors. A. C. Evans, E. C. Hastings and E. B. Hart. Gov. Pub.	869
Cheese of Cheddar Type, Relation of Action of Certain Bacteria to Ripening of. E. B. Hart, E. C. Hastings, E. M. Flint and A. C. Evans. Gov. Pub.	869
Chemical Abstracts, Index to. Editorial.	2
Chemical Abstracts, Resignation of A. M. Patterson, Editor of. Editorial.	794
Chemical Societies in New York City. Program for 1914—1915 Season.	961
Chemical Trade between Germany and the U. S. in 1913. B. C. Hesse. 274; M. L. Hamlin.	1032
Chemical Trade (Foreign) of Canada, 1912 and 1913. Note.	351
Chemical Trade (Foreign) of Canada, 1912 and 1913. Note.	351
Chemical Trade of the U. S. in 1912 and 1913. Note.	690
Chemicals, Guaranteed. Note. V. Lenher.	603
Chemists in Brazil, The. Address.	260
Chemists' Building of Laboratories in. Note.	441
Chemists' Club, The. Address. W. L. Dudley.	467
Chemists (German), What Did We Learn in America? Translation. B. Rassow.	32
Chlorine-Bleaching Flue, Some Chlorine Compounds of. C. A. U. U. 908	
Chlorine, Free, Effect of Ferric Salts and Nitrites on the Ortho-Tolidine and Starch-Iodine Tests for. J. W. Ellms and S. J. Hauser.	553
Choline Type, Preparation of Compounds of the, Including Preparation of Monacetate of $\alpha$ , $\beta$ -Dioxy- $\beta$ -Methyl Butane. G. A. Menge. Gov. Pub.	963
Chromium and Manganese in Iron and Steel, The Determination of. F. C. Daniels.	658
Chrysophanic Acid Reactions and Its Detection in Complex Medicinal Preparations. E. M. Bailey.	320
Cinematograph in Research. Note.	430
Cite, Note on Determination of. F. L. Dodge.	863
Cities: The Broader Applications of Chemistry by the Municipality. H. W. Mahr.	1030
Citrate, "Neutral" Ammonium, Preparation of. E. D. Eastman and J. H. Hildebrand.	577
Citrate Solution, Neutral Ammonium, An Exact and Easy Method for Preparing. J. M. McCandless.	921
Citrate Solutions, Comparison of Neutral Ammonium, Sodium, and $N/10$ Citric Acid. P. Rudnick, W. B. Derby and W. S. Latshaw.	486
Clay Filters and Certain Salt Solutions, The Action between. W. B. Hicks.	829
Clay Products of the U. S. J. Middleton. Gov. Pub.	1043
Coal Calorimeter, A New. Note.	807
Coal, by the Canadian Method. Note.	777
Coal Exports, British, in First Half of 1914. Note.	509
Coal Field, Geology and Coal Resources of the Sierra Blanca, Lincoln and Otero Counties, New Mexico. C. H. Wegemann. Gov. Pub.	964
Coal Fields in Idaho, Washington and Oregon. E. G. Woodruff and C. E. Lester.	785
Coal Mines, Gases Found in. G. A. Burrell and F. M. Seibert. Gov. Pub.	521
Coal near Thompson, Grand County, Utah. E. R. Clark. Gov. Pub.	964
Coal near Wales, V. O. Kress. Gov. Pub.	964
Coal, Origin of. D. White and R. Thiessen. Gov. Pub.	964
Coal Output of the U. S. in 1913. Note.	862
Coal: Production of Anthracite in 1913. E. W. Parker. Gov. Pub.	1041
Coal, Relation of Composition of Ash in, to its Fusing Temperature. O. W. Palmenberg. 277; Note. J. H. K. Burgwin.	694
Coal Resources and General Geology of the Pound Quadrangle of Virginia and Kentucky. C. Butts. Gov. Pub.	964
Coal Resources of a Part of Northeastern Mo. F. C. Greene. Gov. Pub.	964
Coal: Rhode Island Anthracite. G. H. Ashley. Gov. Pub.	964
Coal, Spontaneous Combustion of, in Mines. Note.	350
Coal Storage and Gas Manufacture. Note.	596
Coal, Study of the Oxidation of. H. C. Porter and O. C. Ralston. Gov. Pub.	1043
Coal Tar Chemical Industry in the U. S. Recommendations of the N. Y. Section of the A. C. S. on the Enlargement of the. B. C. Hesse.	972
Coal Tar Cresote, Paraffin Bodies in, and Their Bearing on Specifications. S. R. Church and J. M. Weiss.	396
Coal Tar Pitches, Ultimate Analyses of. C. R. Downs.	206

and the Oxidation of Sulfur Compounds of Coal, and of Nitrogen	812
Coal Trade, Australian. Note.	892
Coal, Utilization of, in Alaska. Gov. Pub.	698
Coal, Weathering of the Pittsburgh Bed at Experimental Mine at Bruceton, Pa. H. C. Porter and A. C. Fieldner. Gov. Pub.	321
Colloids, Preparation of Metallic, by Reduction of the Oxide. H. T. Kalmus.	115
Coke, American Record Production in 1913. Note.	107
Coke and Gas Plants, Disposal of Residuals in. Note.	693
Coke, Gas, Steam Production of. Note.	957
Coke Ovens, By-Product, in Russia. Note.	512
Coke Ovens, Canadian. Note.	597
Coke Ovens, Temperature Conditions in. Note.	956
Coking, in the Powell Mountain, Scott County, Va. M. R. Campbell.	964
Colloids' Lament. The. Poem. Ellwood Hendrick.	357
Color Camera, A Convenient. C. M. Clark.	1012
Comimeter, Sturges', and Lovibond's Tintometer, Conversion Curve for.	323
Combustible and Explosive Mixtures of Gases and Air, Lower Limits of.	191
Combustion of Gas, Partial and Intermittent. E. E. Somermeier.	374
Combustion of Coal and Silver Surfaces. Note.	698
Commerce, Gov. Pub.	698
Commission on Industrial Relations. Editorial. W. A. Hamor.	274
Concrete, Electric Currents in. Note.	351
Concrete, Impermeability, Factors Involved in. Editorial.	1033
Concrete, Paint Films as Protective Coatings for. E. E. Ware and S. M. Schott.	184
Conservation of Natural Resources in Relation to Business. J. J. Conner.	331
Consular Report Abstracts. March, 445 and 522; April, 523; May, 610; June, 699; July, 786; August, 807; September, 965; October, 1043	
Copper Alloys, Commercial, Approximate Melting Point of. U. S. Bureau of Standards. Abstract.	164
Copper in Steel, Cast Iron and Alloy Steels, Rapid Determination of. W. B. Price.	170
Copper. Note on Electrolytic Determination of. H. Cloukey.	265
Copper Production in the U. S. in 1913. B. S. Butler. Gov. Pub.	699
Copper Titrations, Iodine Recovered from Waste Liquor in. G. Torossian.	83
Copper Wire Tables. Gov. Pub.	444
Cotton as a Factor in Determining the Degree of Soundness of. H. J. Besley and G. H. Baston. Gov. Pub.	869
Corrosion of Iron by Dissolved Oxygen. Note.	596
Cotton, Classification and Grading of. D. E. Earle and W. S. Dean.	869
Cotton Cloth, Chemistry of the Bleaching of. J. C. Hehden.	714
Cotton Goods. R. M. Odell. Gov. Pub.	608
Cotton, Tests of Waste, Tensile Strength and Bleaching Qualities of Different Grades of. W. L. Cobb. Gov. Pub.	445
Cotton and Fibre, Possible Reactions of. M. A. Wells.	445
Cottonseed Products and their Competitors in Northern Europe. E. W. Thompson. Gov. Pub., 698; Part 2, Edible Oils.	964
Cream of Tartar, Crystallization of, in Fruit of Grapes. W. B. Creosote, Coal Tar, Paraffin Bodies in, and their Bearing on Specifications. S. R. Church and J. M. Weiss.	608
Cryolite and Fluorspar, Production of, in 1913. E. F. Burchard.	396
Cyanamide, Analysis of Fertilizers Containing. H. W. Hill and W. S. Brinsmaid.	1042
Cyanamide, Analysis, Present State of the. E. J. Franke.	1032
Cyanamide, Recent Increase in Production of. Note.	20
Cyanides, the Alkali and Hydrocyanic Acid, New Method for the Determination of. G. E. F. Lundell and J. A. Bridgman.	415
DENSITY and Volumetric Tables, Standard. Gov. Pub.	554
Dextrin, Solubility of. W. K. Lewis.	522
Diatom of Alfalfa, An Investigation of, and the Effect of Rapid Curing upon the Food Value of Alfalfa. R. C. Shuey.	308
Diesel Engine, Italian Auxiliary Marine. Note.	910
Disinfectants, A Proposed New Standard Loop for Use in Bacteriological Tests of. A. D. St. John.	781
Disinfectants, New Method for Determining Value of. C. A. Duyser.	940
Drug Analysis, Studies in Synthetic. I. Estimation of Acetanilide and Phenacetin in Admixtures. W. O. Emery.	198
H. Estimation of Antipyrin. W. O. Emery and S. Falkin.	651
Drug, Robert Kennedy Standard of. E. Guaden.	687
Drug Products, Patent and Proprietary Medicines, Surgical Instruments and Dental Supplies, South American Markets for. E. A. Hayer. Gov. Pub.	869
Drugs. Commercial Patent in. H. M. Adams.	671
Drugs. Estimation of Podophyllum Resin. W. M. Jenkins.	748
Drugs. Ferric Alum Estimation of Casein. H. V. Army and H. H. Schaefer.	753
Drugs. Iodine in Tablets. A. W. Bender.	584
Drugs. Patent Medicine in Great Britain. Note.	954
Drying Oven Temperature, The Non-Uniformity of. L. H. Bailey.	856
Dudley, William Lofland. Baskerville.	346
Dye, Robert Kennedy Standard of. E. Guaden.	346
Dye, R. H. Southland Standard of. E. Guaden.	346
Dye, Preservation and Rapid Preservation Progress Reports of Experiments in 1913. Gov. Pub.	786
Dye. Exploisability of. H. H. Brown and D. J. Price.	1039
Dye Industry, Analysis of the Coal Tar. Editorial.	972
DYE INDUSTRY, SYMPOSIUM ON AMERICAN. Editorial.	941
Introductory Remarks.	941
Dye. Commercial Patent in. H. M. Adams.	942
Dye. Estimation of Podophyllum Resin. W. M. Jenkins.	945
Dye. Ferric Alum Estimation of Casein. H. V. Army and H. H. Schaefer.	946
Dye. Iodine in Tablets. A. W. Bender.	946
Dye. Patent Medicine in Great Britain. Note.	946
Dye. R. H. Southland Standard of. E. Guaden.	946
Dye. Robert Kennedy Standard of. E. Guaden.	946
Dye. Preservation and Rapid Preservation Progress Reports of Experiments in 1913. Gov. Pub.	946
Dye. Exploisability of. H. H. Brown and D. J. Price.	946
Dye Industry, Analysis of the Coal Tar. Editorial.	946
DYE INDUSTRY, SYMPOSIUM ON AMERICAN. Editorial.	946
Introductory Remarks.	946
Dye. Commercial Patent in. H. M. Adams.	946
Dye. Estimation of Podophyllum Resin. W. M. Jenkins.	946
Dye. Ferric Alum Estimation of Casein. H. V. Army and H. H. Schaefer.	946
Dye. Iodine in Tablets. A. W. Bender.	946
Dye. Patent Medicine in Great Britain. Note.	946
Dye. R. H. Southland Standard of. E. Guaden.	946
Dye. Robert Kennedy Standard of. E. Guaden.	946
Dye. Preservation and Rapid Preservation Progress Reports of Experiments in 1913. Gov. Pub.	946
Dye. Exploisability of. H. H. Brown and D. J. Price.	946
Dye Industry, Analysis of the Coal Tar. Editorial.	946
DYE INDUSTRY, SYMPOSIUM ON AMERICAN. Editorial.	946
Introductory Remarks.	946
Dye. Commercial Patent in. H. M. Adams.	946
Dye. Estimation of Podophyllum Resin. W. M. Jenkins.	946
Dye. Ferric Alum Estimation of Casein. H. V. Army and H. H. Schaefer.	946
Dye. Iodine in Tablets. A. W. Bender.	946
Dye. Patent Medicine in Great Britain. Note.	946
Dye. R. H. Southland Standard of. E. Guaden.	946
Dye. Robert Kennedy Standard of. E. Guaden.	946
Dye. Preservation and Rapid Preservation Progress Reports of Experiments in 1913. Gov. Pub.	946
Dye. Exploisability of. H. H. Brown and D. J. Price.	946
Dye Industry, Analysis of the Coal Tar. Editorial.	946
DYE INDUSTRY, SYMPOSIUM ON AMERICAN. Editorial.	946
Introductory Remarks.	946
Dye. Commercial Patent in. H. M. Adams.	946
Dye. Estimation of Podophyllum Resin. W. M. Jenkins.	946
Dye. Ferric Alum Estimation of Casein. H. V. Army and H. H. Schaefer.	946
Dye. Iodine in Tablets. A. W. Bender.	946
Dye. Patent Medicine in Great Britain. Note.	946
Dye. R. H. Southland Standard of. E. Guaden.	946
Dye. Robert Kennedy Standard of. E. Guaden.	946
Dye. Preservation and Rapid Preservation Progress Reports of Experiments in 1913. Gov. Pub.	946
Dye. Exploisability of. H. H. Brown and D. J. Price.	946
Dye Industry, Analysis of the Coal Tar. Editorial.	946
DYE INDUSTRY, SYMPOSIUM ON AMERICAN. Editorial.	946
Introductory Remarks.	946
Dye. Commercial Patent in. H. M. Adams.	946
Dye. Estimation of Podophyllum Resin. W. M. Jenkins.	946
Dye. Ferric Alum Estimation of Casein. H. V. Army and H. H. Schaefer.	946
Dye. Iodine in Tablets. A. W. Bender.	946
Dye. Patent Medicine in Great Britain. Note.	946
Dye. R. H. Southland Standard of. E. Guaden.	946
Dye. Robert Kennedy Standard of. E. Guaden.	946
Dye. Preservation and Rapid Preservation Progress Reports of Experiments in 1913. Gov. Pub.	946
Dye. Exploisability of. H. H. Brown and D. J. Price.	946
Dye Industry, Analysis of the Coal Tar. Editorial.	946
DYE INDUSTRY, SYMPOSIUM ON AMERICAN. Editorial.	946
Introductory Remarks.	946
Dye. Commercial Patent in. H. M. Adams.	946
Dye. Estimation of Podophyllum Resin. W. M. Jenkins.	946
Dye. Ferric Alum Estimation of Casein. H. V. Army and H. H. Schaefer.	946
Dye. Iodine in Tablets. A. W. Bender.	946
Dye. Patent Medicine in Great Britain. Note.	946
Dye. R. H. Southland Standard of. E. Guaden.	946
Dye. Robert Kennedy Standard of. E. Guaden.	946
Dye. Preservation and Rapid Preservation Progress Reports of Experiments in 1913. Gov. Pub.	946
Dye. Exploisability of. H. H. Brown and D. J. Price.	946
Dye Industry, Analysis of the Coal Tar. Editorial.	946
DYE INDUSTRY, SYMPOSIUM ON AMERICAN. Editorial.	946
Introductory Remarks.	946
Dye. Commercial Patent in. H. M. Adams.	946
Dye. Estimation of Podophyllum Resin. W. M. Jenkins.	946
Dye. Ferric Alum Estimation of Casein. H. V. Army and H. H. Schaefer.	946
Dye. Iodine in Tablets. A. W. Bender.	946
Dye. Patent Medicine in Great Britain. Note.	946
Dye. R. H. Southland Standard of. E. Guaden.	946
Dye. Robert Kennedy Standard of. E. Guaden.	946
Dye. Preservation and Rapid Preservation Progress Reports of Experiments in 1913. Gov. Pub.	946
Dye. Exploisability of. H. H. Brown and D. J. Price.	946
Dye Industry, Analysis of the Coal Tar. Editorial.	946
DYE INDUSTRY, SYMPOSIUM ON AMERICAN. Editorial.	946
Introductory Remarks.	946
Dye. Commercial Patent in. H. M. Adams.	946
Dye. Estimation of Podophyllum Resin. W. M. Jenkins.	946
Dye. Ferric Alum Estimation of Casein. H. V. Army and H. H. Schaefer.	946
Dye. Iodine in Tablets. A. W. Bender.	946
Dye. Patent Medicine in Great Britain. Note.	946
Dye. R. H. Southland Standard of. E. Guaden.	946
Dye. Robert Kennedy Standard of. E. Guaden.	946
Dye. Preservation and Rapid Preservation Progress Reports of Experiments in 1913. Gov. Pub.	946
Dye. Exploisability of. H. H. Brown and D. J. Price.	946
Dye Industry, Analysis of the Coal Tar. Editorial.	946
DYE INDUSTRY, SYMPOSIUM ON AMERICAN. Editorial.	946
Introductory Remarks.	946
Dye. Commercial Patent in. H. M. Adams.	946
Dye. Estimation of Podophyllum Resin. W. M. Jenkins.	946
Dye. Ferric Alum Estimation of Casein. H. V. Army and H. H. Schaefer.	946
Dye. Iodine in Tablets. A. W. Bender.	946
Dye. Patent Medicine in Great Britain. Note.	946
Dye. R. H. Southland Standard of. E. Guaden.	946
Dye. Robert Kennedy Standard of. E. Guaden.	946
Dye. Preservation and Rapid Preservation Progress Reports of Experiments in 1913. Gov. Pub.	946
Dye. Exploisability of. H. H. Brown and D. J. Price.	946
Dye Industry, Analysis of the Coal Tar. Editorial.	946
DYE INDUSTRY, SYMPOSIUM ON AMERICAN. Editorial.	946
Introductory Remarks.	946
Dye. Commercial Patent in. H. M. Adams.	946
Dye. Estimation of Podophyllum Resin. W. M. Jenkins.	946
Dye. Ferric Alum Estimation of Casein. H. V. Army and H. H. Schaefer.	946
Dye. Iodine in Tablets. A. W. Bender.	946
Dye. Patent Medicine in Great Britain. Note.	946
Dye. R. H. Southland Standard of. E. Guaden.	946
Dye. Robert Kennedy Standard of. E. Guaden.	946
Dye. Preservation and Rapid Preservation Progress Reports of Experiments in 1913. Gov. Pub.	946
Dye. Exploisability of. H. H. Brown and D. J. Price.	946
Dye Industry, Analysis of the Coal Tar. Editorial.	946
DYE INDUSTRY, SYMPOSIUM ON AMERICAN. Editorial.	946
Introductory Remarks.	946
Dye. Commercial Patent in. H. M. Adams.	946
Dye. Estimation of Podophyllum Resin. W. M. Jenkins.	946
Dye. Ferric Alum Estimation of Casein. H. V. Army and H. H. Schaefer.	946
Dye. Iodine in Tablets. A. W. Bender.	946
Dye. Patent Medicine in Great Britain. Note.	946
Dye. R. H. Southland Standard of. E. Guaden.	946
Dye. Robert Kennedy Standard of. E. Guaden.	946
Dye. Preservation and Rapid Preservation Progress Reports of Experiments in 1913. Gov. Pub.	946
Dye. Exploisability of. H. H. Brown and D. J. Price.	946
Dye Industry, Analysis of the Coal Tar. Editorial.	946
DYE INDUSTRY, SYMPOSIUM ON AMERICAN. Editorial.	946
Introductory Remarks.	946
Dye. Commercial Patent in. H. M. Adams.	946
Dye. Estimation of Podophyllum Resin. W. M. Jenkins.	946
Dye. Ferric Alum Estimation of Casein. H. V. Army and H. H. Schaefer.	946
Dye. Iodine in Tablets. A. W. Bender.	946
Dye. Patent Medicine in Great Britain. Note.	946
Dye. R. H. Southland Standard of. E. Guaden.	946
Dye. Robert Kennedy Standard of. E. Guaden.	946
Dye. Preservation and Rapid Preservation Progress Reports of Experiments in 1913. Gov. Pub.	946
Dye. Exploisability of. H. H. Brown and D. J. Price.	946
Dye Industry, Analysis of the Coal Tar. Editorial.	946
DYE INDUSTRY, SYMPOSIUM ON AMERICAN. Editorial.	946
Introductory Remarks.	946
Dye. Commercial Patent in. H. M. Adams.	946
Dye. Estimation of Podophyllum Resin. W. M. Jenkins.	946
Dye. Ferric Alum Estimation of Casein. H. V. Army and H. H. Schaefer.	946
Dye. Iodine in Tablets. A. W. Bender.	946
Dye. Patent Medicine in Great Britain. Note.	946
Dye. R. H. Southland Standard of. E. Guaden.	946
Dye. Robert Kennedy Standard of. E. Guaden.	946
Dye. Preservation and Rapid Preservation Progress Reports of Experiments in 1913. Gov. Pub.	946
Dye. Exploisability of. H. H. Brown and D. J. Price.	946
Dye Industry, Analysis of the Coal Tar. Editorial.	946
DYE INDUSTRY, SYMPOSIUM ON AMERICAN. Editorial.	946
Introductory Remarks.	946
Dye. Commercial Patent in. H. M. Adams.	946
Dye. Estimation of Podophyllum Resin. W. M. Jenkins.	946
Dye. Ferric Alum Estimation of Casein. H. V. Army and H. H. Schaefer.	946
Dye. Iodine in Tablets. A. W. Bender.	946
Dye. Patent Medicine in Great Britain. Note.	946
Dye. R. H. Southland Standard of. E. Guaden.	946
Dye. Robert Kennedy Standard of. E. Guaden.	946
Dye. Preservation and Rapid Preservation Progress Reports of Experiments in 1913. Gov. Pub.	946
Dye. Exploisability of. H. H. Brown and D. J. Price.	946
Dye Industry, Analysis of the Coal Tar. Editorial.	946
DYE INDUSTRY, SYMPOSIUM ON AMERICAN. Editorial.	946
Introductory Remarks.	946
Dye. Commercial Patent in. H. M. Adams.	946
Dye. Estimation of Podophyllum Resin. W. M. Jenkins.	946
Dye. Ferric Alum Estimation of Casein. H. V. Army and H. H. Schaefer.	946
Dye. Iodine in Tablets. A. W. Bender.	946
Dye. Patent Medicine in Great Britain. Note.	946
Dye. R. H. Southland Standard of. E. Guaden.	946
Dye. Robert Kennedy Standard of. E. Guaden.	946
Dye. Preservation and Rapid Preservation Progress Reports of Experiments in 1913. Gov. Pub.	946
Dye. Exploisability of. H. H. Brown and D. J. Price.	946
Dye Industry, Analysis of the Coal Tar. Editorial.	946
DYE INDUSTRY, SYMPOSIUM ON AMERICAN. Editorial.	946
Introductory Remarks.	946
Dye. Commercial Patent in. H. M. Adams.	946
Dye. Estimation of Podophyllum Resin. W. M. Jenkins.	946
Dye. Ferric Alum Estimation of Casein. H. V. Army and H. H. Schaefer.	946
Dye. Iodine in Tablets. A. W. Bender.	946
Dye. Patent Medicine in Great Britain. Note.	946
Dye. R. H. Southland Standard of. E. Guaden.	946
Dye. Robert Kennedy Standard of. E. Guaden.	946
Dye. Preservation and Rapid Preservation Progress Reports of Experiments in 1913. Gov. Pub.	946
Dye. Exploisability of. H. H. Brown and D. J. Price.	946
Dye Industry, Analysis of the Coal Tar. Editorial.	946
DYE INDUSTRY, SYMPOSIUM ON AMERICAN. Editorial.	946
Introductory Remarks.	946
Dye. Commercial Patent in. H. M. Adams.	946
Dye. Estimation of Podophyllum Resin. W. M. Jenkins.	946
Dye. Ferric Alum Estimation of Casein. H. V. Army and H. H. Schaefer.	946
Dye. Iodine in Tablets. A. W. Bender.	946
Dye. Patent Medicine in Great Britain. Note.	946
Dye. R. H. Southland Standard of. E. Guaden.	946
Dye. Robert Kennedy Standard of. E. Guaden.	946
Dye. Preservation and Rapid Preservation Progress Reports of Experiments in 1913. Gov. Pub.	946
Dye. Exploisability of. H. H. Brown and D. J. Price.	946
Dye Industry, Analysis of the Coal Tar. Editorial.	946
DYE INDUSTRY, SYMPOSIUM ON AMERICAN. Editorial.	946
Introductory Remarks.	946
Dye. Commercial Patent in. H. M. Adams.	946
Dye. Estimation of Podophyllum Resin. W. M. Jenkins.	946
Dye. Ferric Alum Estimation of Casein. H. V. Army and H. H. Schaefer.	946
Dye. Iodine in Tablets. A. W. Bender.	946
Dye. Patent Medicine in Great Britain. Note.	946
Dye. R. H. Southland Standard of. E. Guaden.	946
Dye. Robert Kennedy Standard of. E. Guaden.	946
Dye. Preservation and Rapid Preservation Progress Reports of Experiments in 1913. Gov. Pub.	946
Dye. Exploisability of. H. H. Brown and D. J. Price.	946
Dye Industry, Analysis of the Coal Tar. Editorial.	946
DYE INDUSTRY, SYMPOSIUM ON AMERICAN. Editorial.	946
Introductory Remarks.	946
Dye. Commercial Patent in. H. M. Adams.	946
Dye. Estimation of Podophyllum Resin. W. M. Jenkins.	946
Dye. Ferric Alum Estimation of Casein. H. V. Army and H. H. Schaefer.	946
Dye. Iodine in Tablets. A. W. Bender.	946
Dye. Patent Medicine in Great Britain. Note.	946
Dye. R. H. Southland Standard of. E. Guaden.	946
Dye. Robert Kennedy Standard of. E. Guaden.	946
Dye. Preservation and Rapid Preservation Progress Reports of Experiments in 1913. Gov. Pub.	946
Dye. Exploisability of. H. H. Brown and D. J. Price.	946
Dye Industry, Analysis of the Coal Tar. Editorial.	946
DYE INDUSTRY, SYMPOSIUM ON AMERICAN. Editorial.	946
Introductory Remarks.	946
Dye. Commercial Patent in. H. M. Adams.	946
Dye. Estimation of Podophyllum Resin. W. M. Jenkins.	946
Dye. Ferric Alum Estimation of Casein. H. V. Army and H. H. Schaefer.	946
Dye. Iodine in Tablets. A. W. Bender.	946
Dye. Patent Medicine in Great Britain. Note.	946
Dye. R. H. Southland Standard of. E. Guaden.	946
Dye. Robert Kennedy Standard of. E. Guaden.	946
Dye. Preservation and Rapid Preservation Progress Reports of Experiments in 1913. Gov. Pub.	946
Dye. Exploisability of. H. H. Brown and D. J. Price.	946
Dye Industry, Analysis of the Coal Tar. Editorial.	946
DYE INDUSTRY, SYMPOSIUM ON AMERICAN. Editorial.	946
Introductory Remarks.	946
Dye. Commercial Patent in. H. M. Adams.	946
Dye. Estimation of Podophyllum Resin. W. M. Jenkins.	946
Dye. Ferric Alum Estimation of Casein. H. V. Army and H. H. Schaefer.	946
Dye. Iodine in Tablets. A. W. Bender.	946
Dye. Patent Medicine in Great Britain. Note.	946
Dye. R. H. Southland Standard of. E. Guaden.	946
Dye. Robert Kennedy Standard of. E. Guaden.	946
Dye. Preservation and Rapid Preservation Progress Reports of Experiments in 1913. Gov. Pub.	946
Dye. Exploisability of. H. H. Brown and D. J. Price.	946
Dye Industry, Analysis of the Coal Tar. Editorial.	946
DYE INDUSTRY, SYMPOSIUM ON AMERICAN. Editorial.	946
Introductory Remarks.	946
Dye. Commercial Patent in. H. M. Adams.	946
Dye. Estimation of Podophyllum Resin. W. M. Jenkins.	946
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Dye. Iodine in Tablets. A. W. Bender.	946
Dye. Patent Medicine in Great Britain. Note.	946
Dye. R. H. Southland Standard of. E. Guaden.	946
Dye. Robert Kennedy Standard of. E. Guaden.	946
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Introductory Remarks.	946
Dye. Commercial Patent in. H. M. Adams.	946
Dye. Estimation of Podophyllum Resin. W. M. Jenkins.	946
Dye. Ferric Alum Estimation of Casein. H. V. Army and H. H. Schaefer.	946
Dye. Iodine in Tablets. A. W. Bender.	946
Dye. Patent Medicine in Great Britain. Note.	946
Dye. R. H. Southland Standard of. E. Guaden.	946
Dye. Robert Kennedy Standard of. E. Guaden.	946
Dye. Preservation and Rapid Preservation Progress Reports of Experiments in 1913. Gov. Pub.	946
Dye. Exploisability of. H. H. Brown and D. J. Price.	946
Dye Industry, Analysis of the Coal Tar. Editorial.	946
DYE INDUSTRY, SYMPOSIUM ON AMERICAN. Editorial.	946
Introductory Remarks.	946
Dye. Commercial Patent in. H. M. Adams.	946
Dye. Estimation of Podophyllum Resin. W. M. Jenkins.	946
Dye. Ferric Alum Estimation of Casein. H. V. Army and H. H. Schaefer.	946
Dye. Iodine in Tablets. A. W. Bender.	946
Dye. Patent Medicine in Great Britain. Note.	946
Dye. R. H. Southland Standard of. E. Guaden.	946
Dye. Robert Kennedy Standard of. E. Guaden.	946
Dye. Preservation and Rapid Preservation Progress Reports of Experiments in 1913. Gov. Pub.	946
Dye. Exploisability of. H. H. Brown and D. J. Price.	946
Dye Industry, Analysis of the Coal Tar. Editorial.	946
DYE INDUSTRY, SYMPOSIUM ON AMERICAN. Editorial.	946
Introductory Remarks.	946
Dye. Commercial Patent in. H. M. Adams.	946
Dye. Estimation of Podophyllum Resin. W. M. Jenkins.	946
Dye. Ferric Alum Estimation of Casein. H. V. Army and H. H. Schaefer.	946
Dye. Iodine in Tablets. A. W. Bender.	946
Dye. Patent Medicine in Great Britain. Note.	946
Dye. R. H. Southland Standard of. E. Guaden.	946
Dye. Robert Kennedy Standard of. E. Guaden.	946
Dye. Preservation and Rapid Preservation Progress Reports of Experiments in 1913. Gov. Pub.	946
Dye. Exploisability of. H. H. Brown and D. J. Price.	946
Dye Industry, Analysis of the Coal Tar. Editorial.	946
DYE INDUSTRY, SYMPOSIUM ON AMERICAN. Editorial.	946
Introductory Remarks.	946
Dye. Commercial Patent in. H. M. Adams.	946
Dye. Estimation of Podophyllum Resin. W. M. Jenkins.	946
Dye. Ferric Alum Estimation of Casein. H. V. Army and H. H. Schaefer.	946
Dye. Iodine in Tablets. A. W. Bender.	946
Dye. Patent Medicine in Great Britain. Note.	946
Dye. R. H. Southland Standard of. E. Guaden.	946
Dye. Robert Kennedy Standard of. E. Guaden.	946
Dye. Preservation and Rapid Preservation Progress Reports of Experiments in 1913. Gov. Pub.	946
Dye. Exploisability of. H. H. Brown and D. J. Price.	946
Dye Industry, Analysis of the Coal Tar. Editorial.	946
DYE INDUSTRY, SYMPOSIUM ON AMERICAN. Editorial.	946
Introductory Remarks.	946
Dye. Commercial Patent in. H. M. Adams.	946
Dye. Estimation of Podophyllum Resin. W. M. Jenkins.	946
Dye. Ferric Alum Estimation of Casein. H. V. Army and H. H. Schaefer.	946
Dye. Iodine in Tablets. A. W. Bender.	946
Dye. Patent Medicine in Great Britain. Note.	946
Dye. R. H. Southland Standard of. E. Guaden.	946
Dye. Robert Kennedy Standard of. E. Guaden.	946
Dye. Preservation and Rapid Preservation Progress Reports of Experiments in 1913. Gov. Pub.	946



Flame Standards in Photometry. E. B. Rosa and E. C. Crittenden. Gov. Pub.	435	Gypsum Deposit, A New, in Iowa. G. F. Kay. Gov. Pub.	785
Flavoring Extracts, Manufacture of. E. M. Chace. Gov. Pub.	445	Gypsum Industry in 1913. R. W. Stone. Gov. Pub.	1042
Floats, Effects of Ensilage Process on Solubility of. E. B. Forbes and C. M. Fritz. 222; Note, C. A. Mooers. Gov. Pub.	695	<b>HELIUM</b> , Natural Gasaceous Mixtures Rich in. Note.	166
Flour, and Meal, Spectral Fluct for Water in. J. H. Cox. Gov. Pub.	908	Hemp. L. H. Dewey. Gov. Pub.	698
Flour, Some Characteristics of Chlorine-Bleached. C. A. A. Utt.	908	Hempel Pipettes, Modified. R. P. Anderson.	237
Flour, Testing of, and Milling of Wheat. H. McCormack.	423	Héroult, P. L. V. Obituary.	506
Flour, Wheat, Determination of Salt Soluble Proteins in. G. A. Olson. Food and Drug Chemists, Standards of. Address. E. Gudeman.	211	Hydrocarbons of Utah—A Correction. C. Bardwell, B. A. Berryman, T. B. Brighton, K. D. Kuhre.	865
Foodstuffs, Hydrogenated Fats as. Note.	691	Hydrocyanic Acid and the Alkali Cyanides. New Method for the Determination of. G. E. F. Lundell and J. A. Bridgman.	554
Flow Recorder, The Fluxograph. Note.	508	Hydrogen in Gas Mixtures, The Determination of, by Means of Colloidal Palladium. G. A. Burrell and G. G. Oberfel.	992
Fluorescence of Petroleum Distillates. B. F. Brooks and R. F. Bacon Fluorspar and Cryolite, Production of, in 1913. E. F. Buchard.	623	D. Edwards. Gov. Pub.	1043
Floods, Valuation of. Note. E. Bidel.	1042	Hydrogen Sulfide in Water, New Apparatus for Determination of. G. B. Frankforter.	676
Food Analysis, Methods of. Gov. Pub.	265	Hydrometers, Testing of. Gov. Pub.	444
Food and Drug Chemists, Standards of. Address. E. Gudeman.	687	Hygiene and Demography, Transactions 15th International Congress on. Gov. Pub.	443
Foodstuffs, Hydrogenated Fats as. Note.	691	Hypochlorite Disinfection of the Baltimore City Water Supplies, Some Further Results of. A Comparison of the Reduction of the Differing Members of the <i>E. Coli</i> Group. J. B. Thomas and E. A. Sandman.	637
Foreign Commerce of the U. S., Monthly Summary of. Gov. Pub.	964	Hypochlorite of Lime Treatment of a Municipal Water Supply and a Study of Certain Resistant Bacteria. S. J. Thomas.	548
Frachel, Herman. Obituary. C. F. Chandler.	505	<b>ICE</b> , Latent Heat of Fusion of. H. C. Dickinson, D. R. Harper and N. S. Osborne. Gov. Pub.	445
Free Brignetting Investigations, July, 1904—July, 1912. C. L. Wright.	444	Imports and Exports. Gov. Pub.	522
Fuels, Contributions to Economic Geology. Gov. Pub.	444	Incescent Electric Lamps, Standard Specifications for. Gov. Pub.	444
Fuller's Earth. Note.	428	Incubator, A Large, for Laboratory Use. F. A. McDermott.	939
Fungicides: Theoretical Basis for Proportions Used in Commercial Application. Note. J. H. Turtar.	488	Industrial Accidents in Pa. in 1912. W. A. Hamor.	783
Furfural in Cider Vinegar, Investigation of Presence of. A. A. Anderson, 214; Correction.	441	Industrial Chemistry, Some Aspects of. Chandler Foundation Lectures, 1914. L. H. Backlund.	769
Furnace, Blast, Obstructions Removed by Explosives. Note.	349	Industrial Chemistry, Some Economic Aspects of. B. C. Hesse. Correction.	868
Furnace, Production of Temperature Uniformity in an Electric. W. Gray. Gov. Pub.	522	<b>INDUSTRIAL CHEMISTS AND CHEMICAL ENGINEERS DIVISION A. C. S.</b> at 49th Meeting, Cincinnati, April 6 to 10, 1914: Alum Specifications Committee Report.	435
Furnaces, Electric, for Heating Steel. A. Hirsch.	533	Report of Progress by Committee on Quality of Platinum Laboratory Utensils.	510
Furnaces, Electric, for Making Iron and Steel. D. A. Lyon and R. M. Keeney. Gov. Pub.	609	Industrial Conditions in France. Note.	512
Furnace, Experiments with for a Hand-Fired Return Tubular Boiler. S. B. Flagg, G. C. Cook and F. E. Woodman. Gov. Pub.	964	Industrial Processes, Application of Physical Chemistry to. Address. W. F. Rittman.	684
<b>GAS</b> Analysis, Monostat for Use in. H. W. Gilbert.	585	Industrial Relations Commission, Editorial. W. A. Hamor.	274
Gas and Coke Plants, Disposal of Residuals in. Note.	957	Industrial Situation in Great Britain, Some Phases of the. Note.	859
Gas and Oil in Western Part of Olympia Peninsula of Washington. F. Lupton. Gov. Pub.	785	Industries, Balance of Trade in Chemical, between U. S. and Germany. B. C. Hesse, 2, 274; M. L. Hamlin.	1034
Gas and Oil: Mud-laden Fluid Applied to Weld Drilling. J. A. Polard and A. G. Higgin. Gov. Pub.	444	Industries, Chemical, in Japan since 1911. Note.	431
Gas and Oil, Prevention of Waste of, from Flowing Wells in California. F. Arnold and V. R. Garbas. Gov. Pub.	521	Industries, Distribution of. W. A. Hamor.	365
Gas: Carbon Monoxide and Nitric Oxide from Heating and Lighting Burners. Note.	779	Industry, Chemistry as Affecting Profitableness of. G. W. Thompson.	152
Gas Coke, Steam Raising by. Note.	452	Industry, Modern Chemical. Hurter Memorial Lecture. F. Haber.	325
Gas Illuminating, Determination of Ammonia in. J. D. Edwards, 468; Gov. Pub.	609	Inks, Analysis of Printing. J. B. Tuttle and W. H. Smith. Gov. Pub.	659
Gas, Important Process for Purifying from Sulfur Compounds. Note.	262	Insecticide Act of 1910, Rules and Regulations for Carrying out Provisions of. Gov. Pub.	869
Gas Industry, Scientific Tendency of. W. R. Addicks.	1032	Insecticide, Arsenate of Lead as an, against the Tobacco Horn-worms in the Dark-Tobacco District. A. C. Morgan and D. C. Parman.	698
Gas, Instruments for Testing. Note.	1032	Insecticide Law, California, The Workings of the. G. P. Gray.	590
Gas, Lead Acetate Test for Hydrogen Sulfide in. R. S. McBride and J. D. Edwards. Gov. Pub.	1043	Insecticide, Valuation of Lime-Sulfur as an. H. V. Tartar.	313
Gas Manufacturing and Coal Storage.	596	Insulating Compound, 30% Hevea Rubber, Tentative Specifications and Analytical Procedure for. Preliminary Report of Joint Committee, 1911-1914. W. A. Del Mar, 75; Note, 514, 515.	1038
Gas Manufacture, from the Point of View of Physical Chemistry. W. F. Rittman.	1027	International Congress of Applied Chemistry, 8th and Certain Industries in U. S., Impressions of. Translation. D. Holde.	35
Gas Manufacture, Recent Improvements in. A. E. Forstall.	499	International Congress of Applied Chemistry, 8th, Travels through U. S. in Conjunction with Translation. R. Hoffmann.	49
Gas Mixtures, Complex, An Apparatus for the Analysis of. G. B. Taylor.	845	International Congress of Applied Chemistry, 9th, St. Petersburg, Aug. 8-14, 1915. Preliminary Announcement by President P. Walden.	606
Gas Mixtures, The Determination of Hydrogen in, by Means of Colloidal Palladium. G. A. Burrell and G. G. Oberfel.	989	International Electrical Congress 1915. Announcement.	171
Gas, Natural, in Canada. Note.	430	Iodine Number of Linseed and Petroleum Oils. W. H. Smith and J. B. Tuttle, 994; Gov. Pub.	784
Gas, Natural, in Hungary. Note.	430	Iodine Recovered from Waste Liquor in Copper Titrations. G. Torossian.	843
Gas, Natural: Wire Gauge Cuzp for Bunsen Burner. G. Torossian.	1037	Iron and Steel, Carbon in, by Barium Carbonate Titration Method. J. R. Cain.	465
Gas, Partial and Intermittent Combustion of. E. E. Sommermeier.	374	Iron and Steel, Determination of Chromium and Manganese in. F. C. T. Dainton.	658
Gas Retorts, Method of Scouring. Note.	509	Iron and Steel, Gases in. Note.	430
Gas Tar, Water, Study of the Composition of. C. R. Downs and J. E. Dean.	366	Iron, Cast, Steel and Alloy Steels, Rapid Method for Copper in. W. B. Price.	170
Gas Testing, Standard Methods of. Gov. Pub.	869	Iron, Corrosion of, by Dissolved Oxygen. Note.	596
Gas Velocities, Pitot Tubes for the Measurement of. A. M. Fairlie.	583	Iron, Critical Ranges of $\lambda_2$ and $\lambda_3$ of Pure. G. K. Burgess and J. J. Crowe. Gov. Pub.	521
Gas Works, Ammonium Chloride, A New By-Product of. Note.	868	Iron, Electric Smelting of, at Hardanger, Norway. Note.	507
Gas Works in Stockholm in 1913. Note.	779	Iron-Furnace Slag, German Utilization of. Note.	694
Gases, Mine and Natural, Sampling and Examination of. G. A. Burrell and F. M. Seibert. Gov. Pub.	444	Iron, Galvanized, A Substitute for. Note.	694
Gasoline Vapor in Natural Gas, The Absorption of, by Fuming Sulfuric Acid. R. P. Anderson and C. J. Engelder.	989	Iron, German Foreign Trade in 1913. Note.	429
Geology, Contributions to Economic. Gov. Pub.	443	Iron in Tomatoes. C. A. Brautlecht and G. Crawford.	1001
Geology, North American for 1913, Bibliography of. J. M. Nickels. Gov. Pub.	964	Iron Nails, Ancient. Note.	260
German Chemical Industry in Russia. Note.	956	Iron Ore, Bate from Stock Band, from Stock B. Coal Mines and on Calcium-Magnesium Ratio in Kentucky Carbonate Ores. A. M. Peter.	497
German Observations on Our Industries (Translations). B. Rassow.	32	Iron, Pig, Cheaper. Inter-State Commerce Commission Decision. Note.	679
Germany and U. S.: Balance of Trade in Chemical Industries. B. H. Hesse, 2, 274; M. L. Hamlin.	1034	Isoprene from Commercial Turpentine. C. H. Herty and J. O. Graham.	803
Glass Analysis, Some Rapid Methods for. E. C. Sullivan and W. C. Taylor.	897	<b>KELP</b> , The Availability of Nitrogen in. J. A. Cullen.	581
Glass, An Efficient Method for Cutting. J. I. Hardy.	238	Kelps, Giant, On Composition of. A. R. Merz.	19
Glass Bottle Industry in the U. S., Present Status of. W. A. Hamor.	509	Kiln, Rotary, Development of, and Its Application to Various Chemical and Metallurgical Processes. R. K. Meade.	754
Glaze, Bottling, Chemical Requirements of. Note.	509	Kjeldahl Distillation Apparatus, New and Improved Form of. A. D. Holmes.	1010
Glazes, Some Leadless Borsilicate, Maturing at about 1100° C. E. T. Montgomery. Gov. Pub.	522		
Glue, Conversion Tables for Commercial. Ginsberg.	1035		
Glue, Wet and Dry, in Wheaten Flour, Physical Factors Which Influence the Percentage of. B. H. Kepner.	481		
Glycerol-Phosphates, Chemistry and Properties of. G. DuBois.	122		
Gold Placers on Wind and Big Horn Rivers, Wyoming. F. C. Schrader. Gov. Pub.	964		
<b>GOVERNMENT PUBLICATIONS.</b> R. S. McBride.	1041		
Grain Dusts, The Explosibility of. H. H. Brown and D. J. Price, 214; Correction.	1039		
Grain Juice, Manufacture of Unfermented, in California. W. V. Cruess and C. J. Hintze.	384		
Graphite Production in 1913. E. S. Bastin. Gov. Pub.	702		
Grease, Tallow, etc., Meaning and Determination of "Impurities" in. C. S. Stillwell.	604		
Grease, Wood, Report of Symposium on Recovery of. C. S. Palmer.	602		
Guano, Bat, On the Composition and Values of. C. F. Miller.	664		
Guaranteed Chemicals. Note. V. Lenher.	603		



## LABORATORY AND PLANT.

Lab., Addition to, in Germany. Note.	603
Lab., English Trade Unions in 1912. Note.	780
Lactalbumin in Cows' Milk, Note on the Precipitation of. W. O. Walker and A. F. Cadenhead.	573
Lamp, The Pentane, as a Working Standard. E. C. Crittenden and A. H. Taylor. Gov. Pub.	521
Laundring, An Investigation into the Chemistry of. W. F. Faragher. List of Weights, Regulations for Enforcement of. Note.	640
Lead Carbonate, Basic Nature of. E. Easton.	382
Lead Contents in Sublimed White Lead—A Calculation. J. A. Schaeffer.	200
Lead, Volumetric Determination of. A. Alder and M. F. Coolbaugh.	398
Lead, White, Constitution of. E. Easton.	202
Leather, Artificial, Destruction of Detritory Factor. Note.	597
Legislation, Effect of, upon Chemical Industries. Presidential Address before Am. Inst. Chem. Eng. T. W. Walker.	71
Lining, Domestic, Fifty Years Ago. Note.	431
Lighting of Rio de Janeiro. Note.	597
Lime and Magnesite for Plants, Comparison of Silicates and Carbonates as Sources of. W. H. MacIntyre and L. G. Willis.	1005
Lime, Nitrogen, Recent Increase in Production of. Note.	692
Lime, Recovery of the Spent, from Causticizing Operations. J. H. Payne.	937
Lime Requirement, The Estimation of, by Means of the Hydroxides of the Alkaline Earths. C. R. Moulton and F. F. Trowbridge.	835
Limestones of the Allentown Quadrangle, A Study of the Dolomitic. S. H. Salisbury, Jr., and G. C. Baker.	487
Lime, Plaster Spate, Theoretical Bases for Proportion Used in Commercial Preparation of. H. V. Tartar.	388
Lime-Sulfur, Valuation of as an Insecticide. H. V. Tartar.	312
Linolic Tetrabromide, Ethyl Ester of, as a Product in the Analysis of Methylated Oil. L. S. Palmer and P. A. Wright.	822
LOEB (MORRIS) MEMORIAL.	343
Address of Acceptance. C. F. McKenna.	343
Presentation Address. L. H. Baekeland.	343
Lubricant for Stopcocks, etc. Note. E. W. Osgerby.	960

## MACHINERY, Automatic, for Placing Powders in Bottles on Net Weight Basis. Note.

Magnesia and Lime for Plants, Comparison of Silicates and Carbonates as Sources of. W. H. MacIntyre and L. G. Willis.	1005
Magnesite Brick or Calcined Magnesite, The Effect of Steam on. R. H. Youngman.	1037
Magnesite, Production of, in 1913. C. G. Yale and H. S. Gale. Gov. Pub.	1042
Magnesium in Calcium Salts, Determination of. J. C. Hostetter.	392
Malt Extract, Laboratory Studies on. H. T. Graber.	403
Maltose, Industrial. L. B. Duryea.	658
Manganese and Chromium in Iron and Steel. F. C. T. Daniels.	658
Manganese and Manganiferous Ores, Production of, in 1913. D. F. Hewett. Gov. Pub.	780
Manganese in Kentucky Soils and Its Possible Significance. O. M. Burchard. Gov. Pub.	520
Manganese Steel, Rolled, Double Scissors Crossing in. Note.	280
Maple and Use in Gas Analysis. H. N. Gilbert.	265
Maple Products, Analysis of: III. Range of Variation of Analytical Values in Genuine Maple Syrups. J. F. Snell and J. M. Scott.	216
IV. Composition of Maple Sugar Sand. J. F. Snell and A. G. Lechhead.	201
Marble Resources of the Juneau, Skagway and Sitka Districts. E. F. Burchard. Gov. Pub.	965
MARKET REPORT. 88, 180, 272, 362, 448, 530, 616, 704, 792, 878, 970, 1051	
Matches, Detection of White Phosphorus in. E. B. Phelps. Gov. Pub.	863
Meat Inspection, Regulations Governing. Gov. Pub.	969
Merchandizing, The Chemist a Growing Factor in. Address. A. V. H. Mory.	689
Mercuric Iodide in Tablets, Determination of. A. W. Bender.	753
Mercury Cathode, Supported, Used in Electrolysis. Note on Unpublished Work. E. LeSueur, 166; Correction.	267
Mercury Engine. A. Note.	511
Mercury Production in 1913. H. D. McCaskey. Gov. Pub.	1043
Mercury Surface, Setting to a Required Height. M. H. Stillman. Gov. Pub.	521
Metallurgy as Applied to Inspection. W. Tassin.	95
Metals and Non-Metals, Except Fuels. Contributions to Economic Geology. Gov. Pub.	609
Metal and Oxide Analysis. I. Nickel Oxide (NiO). Range 600° to 1300° C. K. K. Burgess and P. D. Foote. Gov. Pub.	964
Metals: Gold, Silver, Copper, Lead, etc., Production in 1913. Gov. Pub.	1043
Milk. Recovery of Lactalbumin. E. D. Dunlop. Gov. Pub.	784
Mica, Some Deposits of, in the U. S. D. B. Starrett. Gov. Pub.	964
Microprocessor. G. K. Burgess. Gov. Pub.	444
Microscopes, Micrometer. A. W. Gray. Gov. Pub.	521
Milk and Cream, Cost of Pasteurizing. J. T. Butler. Gov. Pub.	520
Milk and Milk Derivatives, The Specific Heat of. A. R. Johnson and B. W. Hammer.	569
Milk, Application of Refrigeration to the Handling of. J. T. Bowen. Gov. Pub.	963
Milk, Fat in Evaporated, by Rose-Gottlieb Method, Apparatus for. W. Brinsmaid.	324
Milk, Note on the Precipitation of Lactalbumin in. W. O. Walker.	573
Milk and Fat, C. of Cadetizing. J. T. Butler. Gov. Pub.	520
Milk of Porto Rican Cows, Study of. H. J. Lucas, R. J. V. Sarraja and J. R. Benitez.	307
Milk Preparations, Sucrose Estimated in Presence of Lactose and in. Gov. Pakshitt.	22
Milk, Rapid Method for Casein in. W. O. Walker, 131; Correction.	356
Milk, The Composition of, as Shown by Analyses of Samples of Known Purity Made by the Mass. State Board of Health. H. C. Lyne.	899
Mine Accidents—Metal. A. H. Fay. Gov. Pub.	444
Mine Air, Inflammable Gases in. G. A. Burrell and F. M. Seibert. Gov. Pub.	521
Mine Exhibition, at Panama-Pacific Exposition. Note.	782
Mine Fires, Improvised, on an Experimental Scale. H. C. Porter.	146

Mine Gases and Natural Gas, Sampling and Examination of. G. A. Burrell and F. M. Seibert. Gov. Pub.	444
Mine Gases, Report of Committee on Resuscitation from Mine Gases. W. B. Cannon, G. W. Crite, J. Erlanger, Y. Henderson and S. T. Meltzer. Gov. Pub.	964
Mine Inspectors Institute of the U. S. 7th Annual Meeting, Pittsburgh, June 9-13, 1914. W. A. Hamor.	606
Mines, Lake Superior Iron, Fires, E. Higgins. Gov. Pub.	521
Mineral Deposits of Alaska and the Alaskan Mining Industry in 1913. H. Brooks. Gov. Pub.	965
Mineral Deposits of the Kuskataga District, Alaska. A. G. Madden. Gov. Pub.	965
Mineral Production, U. S. for 1912. U. S. Geol. Survey. Note.	165
Mineral Reserves, Oil. How to Make America Industrially Independent. G. Smith. Gov. Pub.	964
Mineral Resources of the U. S., 1912. Metals and Non-Metals. Gov. Pub.	443
Mineral Resources of Alaska, 1913. Gov. Pub.	964
Mineral Resources of the U. S., 1913. Gov. Pub.	609
Mineral Resources of the Yukon Koyukuk Region, Alaska. H. M. Eakin. Gov. Pub.	965
Minerals, Useful, in the U. S. S. Sanford and R. W. Stone. Gov. Pub.	698
Mining Explosives, Specific Gravity Separation Applied to. C. G. Storm and A. L. Hyde. Gov. Pub.	786
Mining in China. Note.	955
Mining in South Africa. Note.	957
Mining: Relative Effects of Carbon Monoxide on Small Animals. G. A. Burrell, F. M. Seibert and L. W. Robertson. Gov. Pub.	444
Moisture Tester for Grain and Other Substances and How to Use It. J. W. Duval. Gov. Pub.	963
Money: Value of Foreign Coins. Gov. Pub.	520
Monroe Doctrine, A European View of. Note.	511
Mortars, Use of Fine Earth in. H. K. Benson and J. S. Herrick.	796
Motor Fuel, The Existence of Free Radicals. Note.	457
Motor Ship "Fionia." Note.	259
Motor Vehicles, Naphthalene as Fuel for. Note.	348
Moving Pictures in Research. Note.	430
Muscular Contractions, Applications of Chemistry to. H. W. Mahr.	1030

NAPHTHALENE as Fuel for Motor Vehicles. Note.	348
National Council for Industrial Safety. Report of Chicago Meeting, October 13 to 15, 1914. W. A. Hamor.	961
"Neutral" Ammonium Citrate, Preparation of. E. D. Eastman and J. H. Hildebrand.	577
New Publications. Gov. Pub.	614, 702, 780, 875.
New Section Added to Journal. (Editorial).	366
NICHOLS MEDAL AWARD.	339
Address of Acceptance: The Existence of Free Radicals. Note.	339
Presentation Address. B. C. Hesse.	339
Nichols Medal, The. Editorial. T. J. Parker.	274
Nit. Note on Detection of, in Fats. R. H. Kerr.	207
Nitrate, Sodium, and Ammonium Sulfate in 1913. Note.	693
Nitrates, Excessive Quantities of, in Certain Colorado Soils. W. P. Headen.	586
Nitric Acid, Concentrated, in Norway. Consular Note.	532
Nitrites and Ferric Salts, Effect of, on the Ortho-Tolidine and Starch-Iodide Tests for Free Chlorine. J. W. Ellis and S. J. Hauser.	553
Nitrogen: A New and Improved Form of Kjeldahl Distillation Apparatus. A. D. Holmes.	1010
Nitrogen Fixation in Scandinavia. Note.	163
Nitrogen in Kelp, The Availability of. J. A. Cullen.	581
Nitrogen in Steel, Improved Method for. L. E. Barton.	1012
Nitrogen, Oxidation of, and of the Sulfur Compounds of Coal in the Bomb Calorimeter, and the Correction To Be Applied in Determining the Heating Value of Coal. S. H. Regester.	812
NOTES AND CORRECTIONS.	82, 166, 263, 353, 440, 517, 601, 690, 782, 863, 958, 1036

OBITUARIES.	346, 505, 782, 856
Oil, River, Chemical Studies of the Pollution of. E. B. Phelps.	682
Gov. Pub.	963
Oil and Gas Fields in Wayne and McCreary Counties, Ky., Reconnaissance of. M. J. Munn. Gov. Pub.	785
Oil and Gas in Western Part of Olympia Peninsula of Washington. C. F. Lupton. Gov. Pub.	785
Oil and Gas: Mud-laden Fluid Applied to Well Drilling. J. A. Pollard and A. G. Higgins. Gov. Pub.	521
Oil and Gas: Presence of Waste from Lignum in California. R. Arnold and V. R. Garfias. Gov. Pub.	521
Oil and Gas, Waste of, in the Mid-Continent Fields. R. S. Blatchley. Gov. Pub.	964
Oil, Cottonseed, Ethyl. Estimation of Lactalbumin as a Product in the Analysis of. L. S. Palmer and P. A. Wright.	822
Oil, Examination of Chinese Wood. E. E. Ware and C. L. Schumann.	806
Oil: Fluorescence of Petroleum Distillates. B. T. Brooks and R. F. Bacon.	623
Oil: Hydrogen Plant in Norway. Trade Note.	165
Oil in Australia. Note.	779
Oil, Mineral, Exports of U. S. Note.	957
Oil Mixtures, Fish and Vegetable, Properties of. G. F. Williams and A. Theodos. Gov. Pub.	521
Oil: Notes on the Composition of Mid-Continental Petroleum. F. W. Bushong.	888
Oil of Black Sage, Investigations on. Burke and C. C. Scallion.	804
Oil: Reasons for One Cause of Low Results in Assay of. H. W. Redfield.	401
Oil, Pine, The Chemistry of. M. Toch.	720
Oil, Raw Linsed, from North American Seeds. Standard Specifications for. Report of Committee, D. 1903-1913 of Am. Soc. for Testing Materials.	164
Oil Recovery in California, Methods of. R. Arnold and V. R. Garfias. Gov. Pub.	786
Oil: Resources of the United Empire. Note.	596
Oil Shale of Northwestern Colorado and Northeastern Utah. E. J. Woodruff and D. T. Day. Gov. Pub.	785
Oil, Sperm, Imports during 1913. Note.	429
Oil: Studies of Crude Petroleum from Biorius, Formosa. T. Katayama.	469

- Oil, White. Note. 349
- Oils, Certain Essential, and Camphor, Rapid Method for Determination of, When in Solution in Alcohol. W. B. D. Pennington and W. W. Randall. 926
- Oils, Essential, as Preservatives of Cane Sugar Solutions. C. B. Cochran and J. H. Perkins. 304
- Oils, Essential, as Preservatives of Starch Syrups. C. B. Cochran and J. H. Perkins. 306
- Oils, Fats, etc., Determination of Acetyl Number of. E. B. Holland. 482
- Oils, Flash Point of: Methods and Apparatus for Its Determination. T. C. Allen and A. S. Crossfield. Gov. Pub. 609
- Oils, Hydrogenated, Analytical Constants of. C. Ellis. 117
- Oils, Lined and Petroleum, Iodine Number of. W. H. Smith and J. H. Tuttle. 784
- Oils, Lubricating, Specifications for. Gov. Pub. 699
- Oils of the Coniariae: A. W. Schorger. I—The Leaf and Twig Oils of Cuban and Longleaf Pines and the Cone Oil of Longleaf Pine. 723
- II—The Leaf and Twig, and Bark Oils of White Fir. 809
- III—The Leaf and Twig, and the Cone Oils of Western Yellow Pine and Sugar Pine. 893
- Oils: Specific Heat of California Petroleum. H. E. Wales. 727
- Correction. 1039
- Oil: Meeting, from Gov. Pub. 171
- Opportunities, On Our. Editorial. 794
- Ore Deposits of Northeastern Washington. H. Bancroft. Gov. Pub. ORIGINAL PAPERS, 3, 91, 184, 277, 366, 452, 533, 619, 706, 795, 882, 976
- Orange Peel, Composition of. H. J. Kressmann. 462
- Oven Temperatures, The Non-Uniformity of Drying. L. H. Bailey. 585
- Oxygen Demand of Sewages, The Biochemical. A. Lederer. 882
- Oxygen Requirement of Shell-Fish. P. H. Mitchell. Gov. Pub. 521
- Oysters, Effect of, on Gas Tar on. P. H. Mitchell. Gov. Pub. 850
- Ozonation, Air. Address. M. W. Franklin. 229
- Ozone, Applications of. A. Vosmaer. 619
- Ozone in Ventilation. J. C. Olsen and W. H. Ulrich. 353
- Ozone in Ventilation. L. von Kupper. Abstract by M. W. Franklin. 170
- Ozone. Note. W. Franklin, 82; W. H. Thomson, 170
- Ozone, Water Purification by, with Report of the Ann Arbor Plant. R. W. Pryer, 197. Note, S. W. Powell, 959; M. W. Franklin. 959
- PAINT** Films as Protective Coatings for Concrete. E. E. Ware and S. M. Schott. 184
- Paint, Papers, Constitution of. H. J. Kressmann. 462
- Paint, White Lead, Remarks on. Published in 1810 by N. Webster, Jr. Note. G. W. Thompson. 266
- Papain, Commercial, and Its Assay. H. M. Adams. 669
- Paper: Chemical Utilization of Southern Pine Waste. M. C. Whitely and J. S. Bates. 289
- Paper: Effects of Certain Cooking Conditions in Producing Soda Pulp from Aspen. H. E. Surface. 963
- Paper Industry in India. Note. 431
- Paper Mills: Investigation of Sulfite Digester Explosion at Grand Mère, Quebec. H. O. Keay. 26
- Paper: Preliminary Note on Dyes and Other Products from the Waste Liquor of the Soda Cellulose Process. M. P. Cram. 896
- Paper Pulp, Suitability of Longleaf Pine for. H. E. Surface and R. Cooper. Gov. Pub. 608
- Paper: Recovery of the Spent Lime from Causticizing Operations. J. H. Payne. 937
- Paper, Specifications for Sulfite. Gov. Pub. 609
- Paper: Utilization of Sulfite-Cellulose Waste. Note. 597
- Paraffin Bodies in Coal Tar Cresote and Their Bearing on Specifications. S. R. Church and J. M. Weiss. 396
- Pasteurization, Ability of Streptococci to Survive. S. H. Ayers and W. T. Johnson, Jr. Gov. Pub. 869
- Patent Situation, The Present. Address. M. Toch. 677
- PATENTS** (see separate heading below).
- Peanut Butter, Some Data on. C. A. A. Utt. 746
- Peat Analyses of Different Grades of Commercial Peat. J. C. Diggs. 310
- Peat, Production of, in 1913. C. A. Davis. Gov. Pub. 1041
- Pentrometer, Asphalt, New Electrically Controlled and Timed. Effect on Penetrations of Variations in Standard Needles. H. W. Mahl. 133
- Pennington, Russell S. Obituary. 782
- PERKIN MEDAL AWARD. 155
- Address of Acceptance. J. W. Hyatt. 153
- Chairman's Address. G. W. Thompson. 155
- Personal Reminiscences. F. Vanderpool. 161
- Presentation Address. C. F. Chandler. 156
- Permeameter, Experimental Study of the Koepsel. C. W. Burrows. W. Pub. 1043
- PERSONAL NOTES.** 83, 172, 267, 356, 442, 518, 607, 697, 783, 868, 961, 1039
- Petroleum, Crude, from Bioritzi, Formosa. T. Katayama. 469
- Petroleum Distillates, Fluorescence of. B. T. Brooks and R. F. Bacon. 623
- Petroleum in Argentine, Engineering Report on. Note. 352
- Petroleum Industry, Problems of. I. C. Allen. Gov. Pub. 609
- Petroleum, Mahone, Its Recent Origin and the Origin of Petroleum in General. C. Mahery. 101
- Petroleum, Notes on the Composition of Mid-Continental. F. W. Bushong. 888
- Petroleum Technology. Gov. Pub. 444
- Petroleum of California, Physical and Chemical Properties of. I. C. Allen, W. A. Jacobs, A. S. Crossfield and R. B. Matthews. Gov. Pub. 609
- Petroleum, Specific Heat of California. H. E. Wales. 727
- Correction. 1039
- Phenacetin and Acetanilide in Admixture, Estimation of. W. O. Emery. 665
- Phenol Determined in Presence of Hexamethylenetetramine and Formaldehyde. L. V. Redman, A. J. Weith and F. P. Brock. 205
- Phosphate Deposits, The Great of Colorado. Idaho, Geology of. R. W. Richards and G. B. Mansfield. Gov. Pub. 964
- Phosphate, Ground Mineral, Effects of Ensilage Process on Solubility of. E. B. Forbes and C. M. Fritz, 222. Note, C. A. Mooers. 695
- Phosphate Rock Production in 1913. W. C. Phalen. 784
- Phosphate Rock Reserve Supply, in the U. S. W. H. Waggaman. 464
- Phosphates, Glycero-, Chemistry and Properties of. G. DuBois. 122
- Phosphoric Acid and Phosphates, Alcohol in the Manufacture of. F. J. Fox. 828
- Phosphoric Acid, Committee Report. Fertilizer Division A. C. S. 49th Meeting, Cincinnati. G. Farnham. 514
- Phosphoric Acid in Phosphate Rock, Effect of Ensilage Fermentation and Animal Digestion on the Solubility of. C. A. Mooers, 487. Note, E. B. Forbes, 605; C. A. Mooers. 695
- Phosphoric Acid in Soils, The Strength of Nitric Acid, Period of Extraction, and Ignition as Affecting the Gravimetric Determination of. H. Brauer and G. J. B. G. 1004
- Phosphoric Acid, Reverted, Use of Sodium Citrate for Determination of. A. W. Bosworth. 227
- Photometry, Flame Standards in. E. B. Rosa and E. C. Crittenden. Gov. Pub. 698
- Physical Chemistry, Application of, to Industrial Processes. Address. W. F. Rittman. 684
- Pinene, *d-d*, Some Observations on. Oil of Port Orford Cedar Wood. A. W. Schorger. 631
- Pipette, Modified, Hemperly. R. F. Anderson. 237
- Pitchblende Ores of Colorado, Geology of. E. S. Bastin. Gov. Pub. 443
- Pitches, Coal Tar, Ultimate Analyses of. C. R. Downs. 206
- Pitot Tubes for the Measurement of Gas Velocities. A. M. Fairlie. 583
- Platinum. Note. Conular Report. T. H. Norton. 165
- Platinum in Westphalia. Note. 696
- Platinum Laboratory Utensils, Quality of. Report of Progress by Committee of Industrial Chemists and Chemical Engineers Division. Cincinnati Meeting, A. C. S. W. F. Hillebrand, E. T. Allen, P. H. Walker. 512
- Platinum Ore in Southern Nevada. Note. 957
- Platinum Thefts at University of Kansas and University of Minnesota. 518
- Platinum Thief. Note. Willamette Pulp and Paper Co. 83
- Platinum Ware, Thermo-Electric Method for Determination of Purity of. C. K. Burgess and P. D. Sale. 452
- Pyrimetry, Gov. Pub. 522
- Porcelain Bodies, Viscosity of. A. V. Bleining and P. Tector. Gov. Pub. 445
- Potash Salts. W. C. Phalen. Gov. Pub. 785
- Potash Salts and Other Salines in the Great Basin Region. G. J. Peterson. 869
- Potash Shipments by German Syndicate in 1914. Note. 429
- Potash Shortage, Remedies for. Note. H. A. Huston. 866
- Potash, Topographic Features of Desert Basins of U. S. with Reference to Modality of Occurrence of. E. D. Free. Gov. Pub. 608
- Potassium Salts, Giant Kelps of Pacific Coast as Source of. F. K. Cameron. Gov. Pub. 445
- Potatoes, Oxidases in Healthy and in Curly-dwarf. H. H. Bunzel. 963
- Potatoes, Utilization of, in Europe. E. P. Skinner. Gov. Pub. 698
- Potentiometers, Testing of. F. Wenner and E. Weibel. Gov. Pub. 964
- Power Plants, By-Product Producer Gas, in Germany. Note. 429
- Precious Metals, Production of. Gov. Pub. 608
- Pressure Absolute, Measurement of. W. N. Shaw. Gov. Pub. 599
- Professional Obligations, Some. Presidential Address. American Institute of Chemical Engineers Meeting, Troy, June 17 to 20, 1914. M. C. Whitaker. 521
- Protein, A New Method for Food Value of. G. F. White and A. Thomas. Gov. Pub. 521
- Proteins, Salt Soluble, Determination of, in Wheat Flour. G. A. Olson. 211
- Pyrometer, The, in the Assay Muffle. F. P. Dewey. 405
- Pyrometers: A New Recording Device. Note. 595
- PATENTS, UNITED STATES.** 86, 178, 271, 361, —, 528, 615, 703, 790, 876, 969, 1046
- Acetaldehyde. Baum and Mugdan. 791
- Acetic Acid. Grunstein. 179
- Acid Concentrated by Means of Drying Agent. Collett. 876
- Acid Chloride, Light Sea Water. 876
- Albumins, Restoring Coagulated, to the Original State. Rasche. 271
- Alcohol from Fermented Sulfite Liquor, Purifying. Ekström. 791
- Alkali-Silico Aluminate Richer in Alkali than Feldspar. Cowles. 703
- Alkali Extracts from Silicates. Messerschmitt. 703
- Alkalis Recovered from Silicate Rocks. Gelléri. 178
- Alumina, Making. Kalmus and Savell. 615
- Aluminum and Its Alloys, Purifying. Mellen. 790
- Aluminum Chloride. McAfee. 876
- Aluminum Fluoride. Dorcums. 1049
- Aluminum Nitride. Serpek. 178
- Aluminum Obtained from Silicious Material. McIlhenny. 271
- Aluminum Sulfate Prepared. Schwann. 178
- Aluminum Sucres Treated. Lang. 178
- Ammonia and Compounds of Ammonia. Rothe. 361
- Ammonia, Catalytic Production of. Bosch and Mittasch. 361
- Ammonia, Production of. Bosch, Mittasch and Wegmann. 703
- Ammonium Synthesis, Color Preparation from Its Constituents. Matignon. 615
- Antimony Oxide. Stark. 791
- Arc Lamp Electrode. Little. 87
- Argon and Rare Atmospheric Gases. Bucher. 1050
- Argon, Physical and Chemical Properties. Barstow. 877
- Asphalt from Crude Mineral Oil or Its Residue. Forward. 529
- Batteries, Storage, Nickel Hydroxide for. Edison. 271
- Bisulfate of Soda. Howard. 169
- Bituminous Putty. Levering. 799
- Bleaching, Fat and Oil. Mueller. 179
- Borates, Fer-, Electrolytic Manufacture. Arndt. 791
- Borax and Boric Acid. Fleming. 615
- Boric Acid. Burger. 1050
- Boron Nitride. Heyder. 784
- Brick Refractory. Wessling. 529
- Bromin for Purifying Water from Germs. Riegel. 790
- Caoutchouc, Synthetic. Gross. 703
- Carbon Monoxide, Hydrogen and Nitrogen. Brownlee and Uhlinger. 1050
- Carbon-Remover. Longenecker. 969
- Ceramic, Extraordinary. Hagemann and Baskerville. 271
- Catalyzers, Making. Ellis. 361
- Catalyzers, Preparation of. Ellis. 361
- Cement Floors, Varnish Composition for. Cabot. 1050
- Cement, Portland. Gardner. 877
- Cement Waterproofing Compound, Set-Adjusting. Ellis. 876
- Cement, Water-Repellent. Ellis. 1049
- Cement, Water-Resistant. Ellis. 1049
- Ceramic, Making. Mariner. 529
- Charcoal, Making. Felizart. 529
- Chlorates, Process of Making. Kolsky. 703







27	614	Journal Articles. D. D. Bessinger, 86, 177, 270, 360, 447.	Soils, Inorganic Composition of Some Important American. W. O.	963
27	614	272, 612, 782, 780, 875.	Robinson. Gov. Pub.	963
27	614	Recorder, Flow, The Fluxograph.	508	Soils, Kentucky, The Occurrence of Manganese in, and Its Possible
27	614	Refractory Elements, Melting Points of. G. K. Burgess and R. G.	508	Significance. O. M. Shedd.
27	614	Waltenberg. Gov. Pub.	445	Soils, Loam, Distribution of Certain Constituents in the Separates of
27	614	Refractory Oxides, Melting Points of Some. C. W. Kanolt. Gov.	445	Soils, Lignite. Note.
27	614	Pub.	445	Soils, Nitrates in Colorado. Editorial. M. X. Sullivan.
27	614	Research in Pure and Applied Chemistry. Van't Hoff Fund for the	445	Soils of Hawaii, Rice; Their Fertilization and Management. W. P.
27	614	Endowment of Communication to Applicants. A. P. Holleman.	445	Kelley. Gov. Pub.
27	614	Research, The Future of Science. Editorial. C. E. K. Mees.	445	Soils, Organic Nitrogen of Some. T. V. R. E. Moore.
27	614	Research: What—Who—Where—Why. Editorial. C. E. Lucke.	618	Soils, Organic Nitrogen of Hawaiian. W. P. Kelley. Gov. Pub.
27	614	Resene, The Effect of, on the Lathering of Soap Solutions. C. H.	618	Soils, Origin of Vanillin in, Vanillin in Wheat and in the Water in
27	614	Herty and H. L. Cox.	895	Which Wheat Seedlings Have Grown. M. X. Sullivan.
27	614	Residue, Acid Stability of, at Slightly Elevated Temperatures. Correc-	895	Soils, Organic Nitrogen of Hawaiian. W. P. Kelley. Gov. Pub.
27	614	tion. C. H. Herty and H. L. Cox.	895	Note, C. C. Fletcher.
27	614	Resin, Podophyllum, Estimation of. W. M. Jenkins.	895	Soils, The Strength of Nitric Acid, Period of Extraction, and Ignition
27	614	Resins in Paleozoic Plants and in Coals of High Rank. D. White.	895	as Affecting the Gravimetric Determination of Phosphoric Acid in.
27	614	Gov. Pub.	895	O. Brauer.
27	614	Resins, Synthetic. L. V. Kedman, A. J. Weith and F. P. Brock, 3.	443	Spelter. Note.
27	614	Note. L. H. Bakeland, 167; Correction, 171; Note.	443	Spelter Production in 1913. C. E. Siebenenthal. Gov. Pub.
27	614	Resistances, Adjustments of the Thomson Bridge in the Measurement	443	Starch, Dry, Soluble in Cold Water, for Use as an Indicator, A Prac-
27	614	of Resistance. J. H. Perkins.	443	tical Method for the Preparation of. R. A. Hapin.
27	614	Road Preservation and Dust Prevention, Progress Reports of Experi-	443	Starch, Dry, Soluble in Cold Water, for Use as an Indicator, A Prac-
27	614	ments in, 1913. Gov. Pub.	443	tical Method for the Preparation of. R. A. Hapin.
27	614	Road Preservation and Dust Prevention, Progress Reports of Experi-	443	Starch, Dry, Soluble in Cold Water, for Use as an Indicator, A Prac-
27	614	ments in, 1913. Gov. Pub.	443	tical Method for the Preparation of. R. A. Hapin.
27	614	Road Preservation and Dust Prevention, Progress Reports of Experi-	443	Starch, Dry, Soluble in Cold Water, for Use as an Indicator, A Prac-
27	614	ments in, 1913. Gov. Pub.	443	tical Method for the Preparation of. R. A. Hapin.
27	614	Road Preservation and Dust Prevention, Progress Reports of Experi-	443	Starch, Dry, Soluble in Cold Water, for Use as an Indicator, A Prac-
27	614	ments in, 1913. Gov. Pub.	443	tical Method for the Preparation of. R. A. Hapin.
27	614	Road Preservation and Dust Prevention, Progress Reports of Experi-	443	Starch, Dry, Soluble in Cold Water, for Use as an Indicator, A Prac-
27	614	ments in, 1913. Gov. Pub.	443	tical Method for the Preparation of. R. A. Hapin.
27	614	Road Preservation and Dust Prevention, Progress Reports of Experi-	443	Starch, Dry, Soluble in Cold Water, for Use as an Indicator, A Prac-
27	614	ments in, 1913. Gov. Pub.	443	tical Method for the Preparation of. R. A. Hapin.
27	614	Road Preservation and Dust Prevention, Progress Reports of Experi-	443	Starch, Dry, Soluble in Cold Water, for Use as an Indicator, A Prac-
27	614	ments in, 1913. Gov. Pub.	443	tical Method for the Preparation of. R. A. Hapin.
27	614	Road Preservation and Dust Prevention, Progress Reports of Experi-	443	Starch, Dry, Soluble in Cold Water, for Use as an Indicator, A Prac-
27	614	ments in, 1913. Gov. Pub.	443	tical Method for the Preparation of. R. A. Hapin.
27	614	Road Preservation and Dust Prevention, Progress Reports of Experi-	443	Starch, Dry, Soluble in Cold Water, for Use as an Indicator, A Prac-
27	614	ments in, 1913. Gov. Pub.	443	tical Method for the Preparation of. R. A. Hapin.
27	614	Road Preservation and Dust Prevention, Progress Reports of Experi-	443	Starch, Dry, Soluble in Cold Water, for Use as an Indicator, A Prac-
27	614	ments in, 1913. Gov. Pub.	443	tical Method for the Preparation of. R. A. Hapin.
27	614	Road Preservation and Dust Prevention, Progress Reports of Experi-	443	Starch, Dry, Soluble in Cold Water, for Use as an Indicator, A Prac-
27	614	ments in, 1913. Gov. Pub.	443	tical Method for the Preparation of. R. A. Hapin.
27	614	Road Preservation and Dust Prevention, Progress Reports of Experi-	443	Starch, Dry, Soluble in Cold Water, for Use as an Indicator, A Prac-
27	614	ments in, 1913. Gov. Pub.	443	tical Method for the Preparation of. R. A. Hapin.
27	614	Road Preservation and Dust Prevention, Progress Reports of Experi-	443	Starch, Dry, Soluble in Cold Water, for Use as an Indicator, A Prac-
27	614	ments in, 1913. Gov. Pub.	443	tical Method for the Preparation of. R. A. Hapin.
27	614	Road Preservation and Dust Prevention, Progress Reports of Experi-	443	Starch, Dry, Soluble in Cold Water, for Use as an Indicator, A Prac-
27	614	ments in, 1913. Gov. Pub.	443	tical Method for the Preparation of. R. A. Hapin.
27	614	Road Preservation and Dust Prevention, Progress Reports of Experi-	443	Starch, Dry, Soluble in Cold Water, for Use as an Indicator, A Prac-
27	614	ments in, 1913. Gov. Pub.	443	tical Method for the Preparation of. R. A. Hapin.
27	614	Road Preservation and Dust Prevention, Progress Reports of Experi-	443	Starch, Dry, Soluble in Cold Water, for Use as an Indicator, A Prac-
27	614	ments in, 1913. Gov. Pub.	443	tical Method for the Preparation of. R. A. Hapin.
27	614	Road Preservation and Dust Prevention, Progress Reports of Experi-	443	Starch, Dry, Soluble in Cold Water, for Use as an Indicator, A Prac-
27	614	ments in, 1913. Gov. Pub.	443	tical Method for the Preparation of. R. A. Hapin

Trade Directory of South America. Gov. Pub.	522	Water Purified by Adsorption. Preliminary Note. M. P. Cram and H. P. Evans.	166
Trade in Chemicals and Chemical Products between Germany and the U. S. in 1913. B. C. Hess.	1034	Water Softener and Storage Tank, A Combination. L. M. Booth.	760
Trade in Chemicals, England's, in 1912 and 1913. Note.	351	Water Softening, Comparative Value of Calcium and Calcium-Magnesium Limes for. E. Bartow and C. Scholl.	189
Trade in Chemicals (Foreign) of Canada, 1912 and 1913. Note.	691	Water: Studies of Self-Purification of Streams. E. B. Phelps. Gov. Pub.	963
Trade in Chemicals, U. S., in 1912 and 1913. Note.	690	Water Supplies, Some Further Results of the Hypochlorite Disinfection of the Baltimore City. A Comparison of the Reduction of the Different Members of the <i>B. Coli</i> Group. J. B. Thomas and E. A. Sandman.	637
Trade Unions, English, in 1912. Note.	780	Water Supply, Hypochlorite of Lime Treatment of a Municipal, and a Study of Certain Resistant Bacteria. S. J. Thomas.	548
Transportation of Chemicals by Water. Note.	349	Water: Surface of the U. S., 1912. Gov. Pub.	965
Tungsten: Colorado Ferberite and the Wolframite Series. F. L. Henshaw and W. T. Schaller. Gov. Pub.	964	Water: The Effect of Ferric Salts and Nitrites on the Ortho-Tolidine and Starch-Iodide Tests for Free Chlorine. J. W. Ellms and S. J. Hauser.	553
Tunnels, Gaseous Impurities in the Air of Railway. A. Seidell and P. W. Meserve. Gov. Pub.	786	Water: The Relation between Aluminum Sulfate and Color in Mechanical Filtration. F. E. Hale.	632
Turpentine, Chemical Utilization of Southern Pine Waste. M. C. Whitaker and J. S. Bates.	289	Water, What is a Safe Drinking? A. J. McLoughlin. Gov. Pub.	786
Turpentine Gum, Study of Authentic Samples of. A. W. Schorger.	541	Water Works Association, Journal of the American. Editorial Book.	365
Turpentine Industry, Wood, Present Status of. E. H. French and J. R. Withrow.	148	Waters, Natural, Determination of Hardness in. C. Bohlmann.	209
Turpentine, Kerosene from Commercial. C. H. Herty and J. O. Graham.	803	Waters of Saratoga Springs, Radioactivity of the. R. B. Moore and C. F. Whittemore.	552
UNIVERSITIES, Some Statistics on German. Note.	350	Waters, Production of Mineral, in 1913, with a Discussion of Their Radioactivity. R. B. Dole. Gov. Pub.	1042
Uranium, Radium and Vanadium Report by U. S. Bureau of Mines. R. B. Moore and K. S. Kithil, Abstract 164; Gov. Pub.	609	Waters, Quality of the Surface, of Washington. W. Van Winkle. Gov. Pub.	965
VACUUM System, Scrubber for Chemical Laboratory. C. Baskerville.	675	Waters, Recent Analyses of Saratoga Mineral. IV. L. R. Milford.	608
Vanadium, Note on Calorimetric Method for. C. R. McCabe.	960	Weather Review, Monthly. Gov. Pub.	869
Vanadium, Uranium and Radium Report by U. S. Bureau of Mines. R. B. Moore and K. L. Kithil, Abstract 164; Gov. Pub.	609	Weights and Measures, Units of. Gov. Pub.	365
Vanillin in Soils, The Origin of Vanillin in Wheat and in the Water in Which Wheat Seedlings Have Grown. M. K. Sullivan.	919	Welfare and Safety Provisions at the Welsbach Company's Plants. H. Lyon, 336; Correction.	441
Velocities, Gas, Pilot Tubes for the Measurement of. A. M. Fairlie.	583	Westinghouse, George. Obituary. W. A. Hamor.	347
Ventilation, Ozone in. J. C. Olsen and W. H. Ulrich.	619	Wheat, Environmental Influences on the Physical and Chemical Characteristics of. J. A. LeClerc and P. A. Yoder. Gov. Pub.	445
VENTILATION SYMPOSIUM.	245	Wheat, Milling of, and Testing of Flour. H. McCormack.	423
Investigation of School Air in N. Y. City. C. Baskerville.	250	Wheat, Vanillin in, and in the Water in Which Wheat Seedlings Have Grown. M. X. Sullivan.	919
Mechanical Problems of Ventilation. D. D. Kimball.	248	White Lead, Constitution of. E. Euston.	202
Physiological Problems of Ventilation. F. S. Lee.	245	White Lead, Sublimed, Lead Contains in. A Calculation. J. A. Schaeffer.	200
The N. Y. State Commission on Ventilation and Its Problems. C. E. A. Winslow.	255	Wood, A. New Method for the Determination of Zinc in Treated. M. H. Bedford and R. Planstiel.	811
Ventilation, Use of Ozone in. L. von Kupffer. Abstract by M. W. Franklin.	353	Wood: Chemical Utilization of Southern Pine Waste. M. C. Whitaker and J. S. Bates.	289
Vinegar, Cider, Investigation of Presence of Furfural in. A. A. Anderson, 214; Correction.	441	Wood, Density of Wood Substances and Porosity of. F. Dunlap. Gov. Pub.	963
Vinegars, So-Called Farmers' Cider, Some Abnormal Factors of. J. C. Diggs.	215	Wood Distillation under Diminished Pressure. M. Adams and C. Hilton.	378
Viscometer, New, for General Scientific and Technical Purposes. E. C. Bingham.	233	Wood, English Processes for Fireproofing. Note.	261
Voltmeter, The Silver. E. B. Rosa, G. W. Vinal and A. S. McDaniel. Gov. Pub.	445	Wood, Hard. Effect of Pressure on Yields of Products in the Destructive Distillation of. R. C. Palmer.	890
Voltmeters, Comparison of the Silver and Iodine, and Determination of Value of the Faraday. G. W. Vinal and S. J. Bates. Gov. Pub.	521	Wood Preservatives, Toxicity of Various. C. J. Humphrey and R. M. Fleming, 128; Note, E. P. Schoch.	603
WATER Analysis, Hypothetical Combinations in. R. B. Dole.	710	Wood, Pulp, Evaluation of. M. L. Griffin. Abstract.	163
Water: A New Seal for Prevention of Aeration in Deaerated Liquids. F. Bachmann.	764	Wood: Relative Resistance of Various Conifers to Injection with Cresote. C. H. Tressdale. Gov. Pub.	963
Water: A Sanitary Survey of White River (Indiana). J. C. Diggs.	639	Wood, The Chemical Evaluation of, for Pulp. M. L. Griffin.	560
Water: Chemical Studies of the Pollution of the Ohio River. E. B. Phelps, 682; Gov. Pub.	963	Wood, The Oil of Port Orford Cedar, and Some Observations on <i>d</i> - $\alpha$ -Pinene. A. W. Schorger.	631
Water: Coastal, Investigation of, in Vicinity of Gulfport and Biloxi, Miss., with Reference to Pollution of Shellfish. R. H. Creel. Gov. Pub.	963	Wood, Treated, Zinc Chloride in. E. Bateman.	16
Water: Comparison of Methods for Oxygen in, in Presence of Nitrite. E. Elvove. Gov. Pub.	963	Wood Turpentine Industry, Present Status of. E. H. French and J. R. Withrow.	148
Water Gas Tar, Study of the Composition of. C. R. Downs and A. L. Dean.	366	Wood Waste, Manufacture of Ethyl Alcohol from. Preliminary Experiments on the Hydrolysis of White Spruce. F. W. Kressman.	625
Water Gas, Thermal Reactions in Carbureting. M. C. Whitaker and W. F. Kittman.	472	Wood: Yields from Destructive Distillation of Certain Hardwoods. L. F. Hawley and R. C. Palmer. Gov. Pub.	963
Water, Mineral, Production in 1912. Note.	781	Wood Grease, Symposium on Recovery of. C. S. Palmer.	602
Water: Modified Apparatus for Putrescibility Test. A. M. Buswell.	325		
Water, New Apparatus for Determination of Hydrogen Sulfide in. C. B. Frankforter.	676	YEAST, Effect of High Temperature on. C. B. Cochran and J. H. Perkins.	480
Water: Note on New Apparatus for Use with Winkler Method for Dissolved Oxygen in. H. L. Shoub. Gov. Pub.	963		
Water, Pollution of Tidal. H. S. Cumming. Gov. Pub.	698	ZINC Chloride in Treated Wood. E. Bateman.	16
Water Power Undertakings in Norway, Further. Note.	692	Zinc in Treated Wood, A New Method for the Determination of. M. H. Bedford and R. Planstiel.	811
Water Purification by Ozone—with Report of the Ann Arbor Plant. R. W. Fryer, 797; Note, S. T. Powell, 959; M. W. Franklin.	959	Zinc Production in Europe in 1913. Note.	595
Water Purification, Test of Gila River Natural Aluminum Sulfate in. D. M. Grosh.	605		













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